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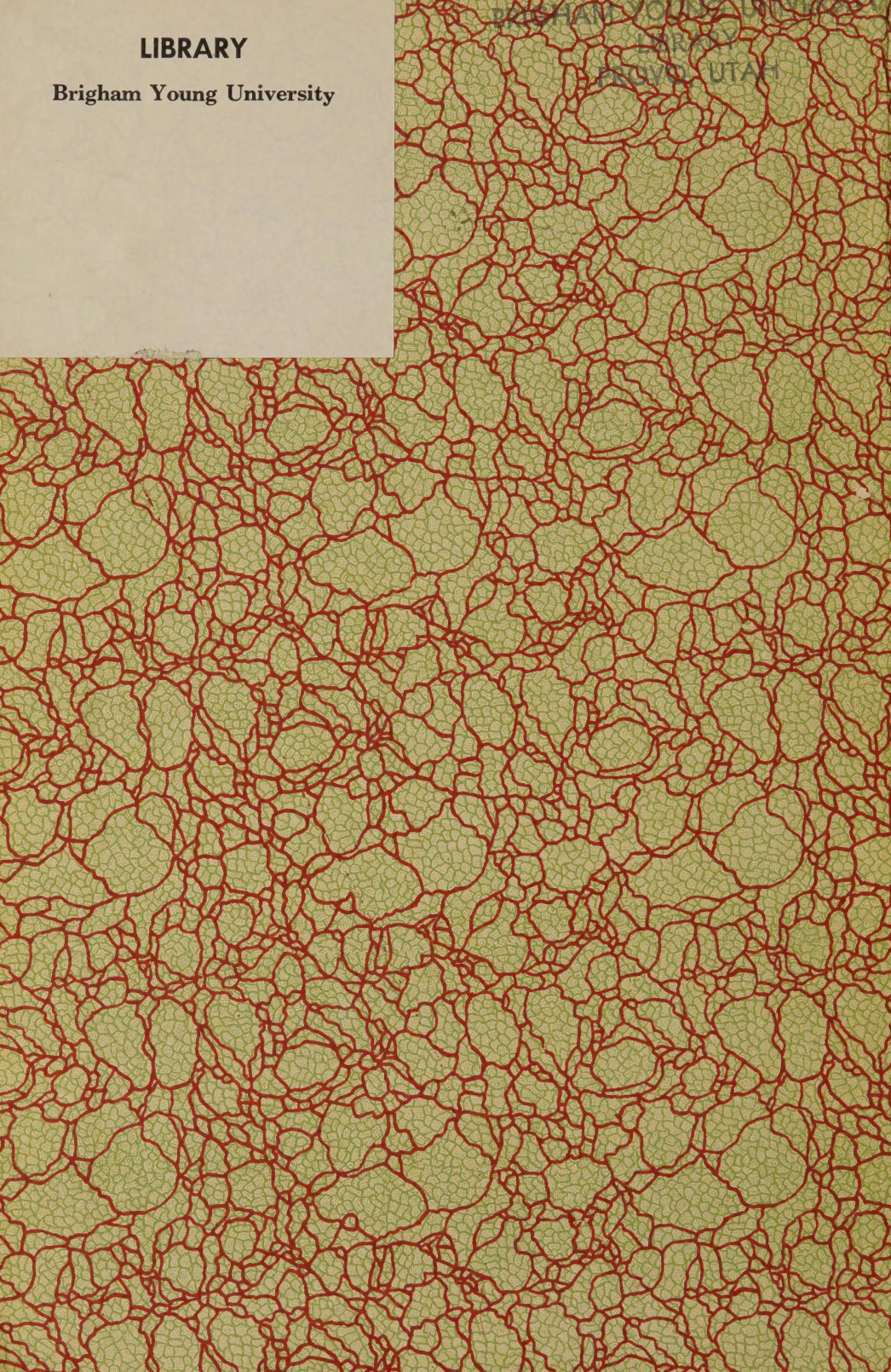

Carl H. Landon
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TRANSACTIONS

OF THE

AMERICAN CERAMIC SOCIETY

VOLUME X.

Containing Papers and Discussions Read at the Meeting Held at Columbus, Ohio, Feb. 3rd, 4th and 5th 1908, With Some Other Contributions.

This Society is not, as an organization, responsible for the statements of facts or opinions expressed in its papers and discussions.

PUBLISHED BY THE SOCIETY
SECRETARY'S OFFICE, COLUMBUS, OHIO
1908

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NOTE BY THE EDITOR.

The last page proof of Vol. X has been corrected. The preliminary matter preceding the papers and discussions was not delivered to me until nearly everything else had been printed. It is now seen that two more pages were allowed for this matter than was necessary. Hence, I will occupy a portion of this space with a note of explanation.

The entire page proof is now in the hands of the printers and most of the sheets for the complete edition of the volume have been printed. The best that could be done now would not give us the bound volumes before the 1st of September and it is doubtful if, even with a good deal of prodding, we can get the volumes through the bindery before the middle of September. This must seem to our members an unnecessarily late date—and it certainly is. The Volume of Transactions ought to be in the hands of the members of the Society within four months after our annual meeting. How can this be accomplished? The editor should be appointed by the trustees at the time of the meeting in February. All papers, drawings, etc., presented at the meeting should be immediately delivered into his hands. Papers not completed should be delivered to him prior to April 1st or go over to the following year. Work upon the ink drawings and engravings and the printing of the papers in galley proof can be begun early in February. By the time the stenographer's transcript of the discussions is received and corrections have been made by the speakers, most of the other matter can be in type. The volume could thus be issued by June 1st.

Contract with me to edit the transactions was made April 17th, and on April 20th there was delivered to me the stenographer's transcript of the discussions and such of the papers as were in the hands of the secretary. Many of the papers could not be obtained until June, and three or four of the papers were not given to me until July. None of the delay in getting out the Volume is chargeable to me except such as has come from inexperience in handling the job, but reviewing the whole matter now, I am prepared to say that with an editor who is free to give his time to the work and who receives his appointment in due season, the Volume of Transactions could be made ready for distribution some time

in May. In making this statement I do not depreciate the amount of work involved, for I have found this more than I supposed.

The best results, of course, as has been pointed out by Prof. Orton, would be obtained by a secretary paid to give his whole time to the affairs of the Society; but as Prof. Orton could not be secured for this position, even were the Society able to pay an adequate salary, and as the Society cannot afford to lose the services which he seems willing to give it gratis, it is the plain duty of the Society to relieve Prof. Orton of as much of the clerical and routine work as he can hire others to do, even though it may necessitate an increase of our annual dues. After my experience in editing Vol. X, I want to say that I consider it an imposition for the Society to place this work upon Prof. Orton, a man burdened with so many duties, but whose enthusiastic interest in the welfare and progress of the Society might lead him to overstrain his powers.

I should say in conclusion that this note is inserted at the last moment to save blank pages, and without the knowledge of Prof. Orton, who is in Colorado.

W. D. Richardson, Editor.

Columbus, Ohio, August 19, 1908.

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LLOYD, HARRY, New Salisbury, Ohio. — Superintendent Colonial Clay & Coal Company.

LOCKE, FREDERICK M., Victor, N. Y. — Manufacturer Porcelain Insulators.

LOCKE, MORTON FIELD, Lima, N. Y.	President and Secretary Lima Insulator Company.
LOWNDES, WILLIAM BLADEN, Mt. Savage, Md.	Supt., Mt. Savage Fire Brick Co.
MCBEAN, ATHOLE, Eddy & Hyde Sts., San Francisco, Cal.	Secy. and Treas., Gladding, McBean & Company.
MCNICOL, JOHN A., East Liverpool, Ohio.	Manager, D. E. McNicol Pottery Co.
MADDISON, ERNEST A., Auburn, Wash.	President, Northern Clay Products Company.
MADDOCK, ARCHIBALD M., Trenton, N. J.	Thomas Maddock & Sons.
MADDOCK, JOHN, Trenton, N. J.	John Maddock & Sons.
MANDLE, I., 3943 Pine St., St. Louis, Mo.	Miner and Shipper of Pottery Clay.
MANDLE, SIDNEY, 3943 W. Pine St. St. Louis, Mo.	Asst. Treas. Mandle-Sant Clay Co.
MANOR, JNO. M., East Liverpool, Ohio.	Mgr., Golding Sons Co.
MARTIN, PETER WRIGHT, 132 Nassau St., New York City.	Vice Pres., American Clay Company.
MASON, FORTUNATUS Q., East Liverpool, Ohio.	Color Manufacturer.
MAYER, ARTHUR ELLIS, 3rd Ave., New Brighton, Pa.	With Mayer Pottery Company.
MELLOR, F. G., Trenton, N. J.	Gen. Mgr., Cook Pottery Company.
MEAKIN, ROBERT J., East Liverpool, Ohio.	Mgr., Hall China Company.
MERRY, CARL EMMETT, 930 W. Illinois St., Urbana, Ills.	Ceramic Student.
METZNER, OTTO, Cincinnati, Ohio.	Supt. of Manufacture, Rookwood Pottery Company.
MIDDLETON, JEFFERSON, 3412 13th St., Washington, D. C.	Statistician, United States Geological Survey.

MILES, JAMES, East Liverpool, Ohio.	Asst. Supt., Homer-Laughlin China Company.
MITCHELL, WALTER CHARLES, Seattle, Wash.	Denny-Renton Clay & Coal Company.
MONTGOMERY, EARLE T., E.M. (in Cer) Columbus, Ohio.	
MOORE, H. W., 96 Patterson St., New Brunswick, N. J.	Assistant Instructor Department of Ceramics, Rutgers Scientific College.
MOREY, D. F., Ottumwa, Iowa.	Mgr., Ottumwa Press Brick & Coal Company.
MORRIS, W. C., St. Louis. Mo.	Vice. Pres. and Gen. Mgr., Christy Fire Clay Company.
MOSES, JAMES, Trenton, N. J.	Mercer Pottery Company.
MUNSHAW, LAMBERT M., Crystal Lake, Ills.	Ceramist, American Terra Cotta and Ceramic Company.
NEALL, HARRY L., B. L., 2206 Hunting Park Ave., Philadelphia, Pa.	
OGAN, MARK, 3131 Pasadena Ave., Los Angeles, Cal.	General Supt. Douglas Clay Products Company.
OGDEN, LESTER, 106 Price St., Columbus, Ohio.	Federal Brick Company.
OUDIN, C. P., Mica, Washington.	Gen. Mgr., American Fire Brick Co.
PATTERSON, J. W., Wellsville, Ohio.	Patterson & Son, Yellowware Potters.
PETERSON, RUDOLPH A., Cleveland, Ohio.	Salesman, The Harshaw, Fuller & Goodwin Company.
PFEIFFER, JACOB, 718 Bryden Road, Columbus, Ohio.	Pres., Logan Clay Products Company.
PHILLIPS, WILLIAM, 609 Haight Ave., Alameda, Cal.	Supt., N. Clark & Sons.
PITZER, G. N., Cherryvale, Kansas.	
PLUSCH, HERMAN A., B. Sc., Rocky Hill, N. J.	Ceramist, Excelsior Terra Cotta Co.
PODMORE, JOSEPH, Troy, N. Y.	Ostrander Fire Brick Company.

POOLE, JOSHUA, East Liverpool, Ohio.	Mgr., Homer-Laughlin China Co.
POPE, CHARLES, Santiago, Chile, S. A., P. O. Box 2369.	
PORTER, ALFRED S., 573 E. 114th St., Cleveland, O.	Editor, "Glass & Pottery World," Chicago.
PORTER, JOHN JERMAIN, Observatory Ave., Station O, Cincinnati, Ohio.	Chemist and Metallurgist.
POST, MALCOLM P., Texarkana, Ark.	Supt., Post Sewer Pipe Company.
POWELL, WILLIAM H., New York, N. Y.	Vice-Pres. Atlantic Terra Cotta Co.
PRESTON, FRANCIS C., 509 Cuyahoga Bldg, Cleveland, O.	Sales Agent. Dover Fire Brick Co.
PURINGTON, DILWYN V., Chamber of Commerce Bldg., Chicago, Ill.	Pres., Purington Paving Brick Co.
PYATT, FRANK E., Box 163, Milltown, N. J.	Tile Maker.
RAMSEY, ANDREW, Mt. Savage, Maryland.	Manufacturer of Enameled Brick.
RANDALL, JAMES E., Indianapolis, Ind.	Associate Editor, "Clayworker."
RANDALL, THEODORE A., Indianapolis, Ind.	Editor, "Clay-Worker."
RAYNOLDS, EDWIN WILLIAM, P. O. Box 189, Cleveland, Ohio.	
REA, WILLIAM J., Buffalo, N. Y.	Supt., Buffalo Pottery Company.
RICHARDSON, CLIFFORD, PH. D., Room 1826 Cortlandt Bldg., 30 Church St., New York City.	Director, New York Testing Laboratory.
RIVERS, WILLIAM EDWARD, Old Bridge, N. J.	Vice-President. Old Bridge Enameled Brick and Tile Co.
ROBINEAU, SAMUEL E., Syracuse, N. Y.	Editor, "Keramic Studio."
ROBINSON, EDWARD WANTON, Hartford, Conn.	Gen. Mgr., Hartford Faience Co.
RODGERS, EBEN, Alton, Ills.	Manager, Alton Paving Brick Co.

ROGERS, GREGORY L., Bessemer, Pa.	Bessemer Limestone Co.
ROESSLER, FRANZ, 100 William St., New York.	Vice-Pres. and Supt., Roessler & Hasslacher Company.
ROWE, JOHN, Zanesville, Ohio.	Asst. Supt., American Encaustic Tiling Company.
SANT, JOHN, East Liverpool, Ohio.	Clay Salesman, Miner and Broker.
SANT, THOMAS HERBERT, East Liverpool, Ohio.	Clay Salesman, Miner and Broker.
SAVAGE, HARLOW DOW, Ashland, Ky.	Treasurer, Ashland Fire Brick Co.
SIMCOE, GEORGE, Victor, N. Y.	Supt., Factory No. 2, Locke Insulator Company.
SIMKINS,, RALPH, St. Louis, Mo.	Mgr., Union Pressed Brick Works.
SINCLAIR, HERBERT, Trenton, N. J.	Gen. Mgr., Star Porcelain Company.
SINGER, LEWIS P., Lilcoln, Cal.	Chemist, Gladding, McBean & Co.
SMITH, AMEDEE M., Portland, Oregon.	Western Clay Manufacturing Co.
SMITH, HARRY W., East Liverpool, Ohio.	Representative of the Roessler & Hasslacher Chemical Company.
SMITH, PERRY A., New Brighton, Pa.	Secy., A. F. Smith Company.
SPEIR, HARRY F., Lewistown, Pa.	Supt., Pennsylvania Pulverizing Co.
STALEY, HOMER FRANCIS, A. B., Uniontown, Pa.	Supt., The McCrum-Howell Co.
STAMM, JOHN, East Liverpool, Ohio.	General Manager National China Company.
STANBERY, GEORGE A., Zanesville, Ohio.	Manager, American Encaustic Tile Company, Ltd.
STEVENSON, WM. G., East Liverpool, Ohio.	Gen. Mgr., Ohio Silica Company.
STULL, RAY T., E. M. (in Cer.) Champaign, Ill.	University of Illinois.

Stowe, Charles B., Cleveland, Ohio.	The Stowe-Fuller Company.
Taylor, William Watts, Cincinnati, Ohio.	President, Rookwood Pottery Co.
Thomas, Chauncey Rapelje, Amherst, Mass.	Ceramic Student.
Thomas, David C., Minerva, Ohio.	Owen Pottery.
Thrall, Charles U., Tottenville, S. I., N. Y.	Supt., Atlantic Terra Cotta Co.
Tone, Frank J., Niagara Falls, N. Y.	Works Mgr., Carborundum Co.
Topping, John Arthur, Bordonia, Rockland Co., N. Y.	
Townsend, Everett, Morrisville, Pa.	National Tile Company.
Trommer, Carl E., 319 E. 57th St., New York City.	
Vodrey, William E., East Liverpool, Ohio.	Gen. Mgr., Vodrey Pottery Co.
Volz, William J., St. Louis, Mo.	Supt., Evens & Howard Fire Brick Company.
Wagner, Fritz, Chicago, Ill.	Northwestern Terra Cotta Co.
Walcott, Benjamin O., Indianapolis, Ind.	Pres., Indianapolis Terra Cotta Co.
Wanka, Louis, Clayton, Wash.	Washington Brick, Lime & Mfg. Co.
Wellington, Arthur J., 235 Franklin St., Boston, Mass.	Richmond Brick Company.
Wells, Harry B., Ironton, Ohio.	Mgr. Orchard Knob Clay Products Company.
Wheat, Howard Irving, 987 Sterling Place, Brooklyn, N. Y.	Ceramic Student.
Whitehead, C. Louis, Trenton, N. J.	Providential Tile Works.
Whitmer, J. D., Cr. E., Covington, Ohio.	Ceramic Student.

WHITTAKER, JOHN L., Trenton, N. J.	Works Mgr., Lenox, Incorporated.
WILL, OTTO W., Perth Amboy, N. J.	Supt., Color Dept., Roessler & Hasslacher Chemical Company.
WILLIAMS, IRA A., M. Sc., Ames, Iowa.	Assistant Professor of Geology, Iowa State College.
WIRT, HERBERT C., Hansen, Mass.	President, Wirt Mfg. Co.
WORCESTER, WOLSEY GARNET, Columbus, Ohio.	Assistant in Clayworking Laboratory, Department of Ceramic Engineering, Ohio State University.
ZEIME, CARL HANS, P. O. Box 244, New Castle, Pa.	
ZIMMERMAN, CLARENCE IRVING, 310 Jefferson Ave., Niagara Falls, N. Y.	Electro-Metallurgist, Carborundum Company.

ANNUAL REPORT OF THE BOARD OF TRUSTEES.

Columbus, Ohio, February 3rd, 1908.

To the Members and Associates of the American Ceramic Society:

We have the honor to submit the following report of the Society's business for the year beginning February 1st, 1907, and ending February 1st, 1908:

VOLUME IX.

Volume IX constitutes much the largest and in some respects the most important volume yet undertaken by the Society. It contains 808 pages, and five unnumbered illustrations, besides a very large number of other illustrations which are numbered and run in with the text.

This volume was undertaken with much energy and pushed vigorously for the first three months after the annual meeting. The articles contributed by Professor Purdy and Mr. Jones were given to us for publication only through the courtesy of the University of Illinois and the Illinois Geological Survey, and they required as a condition that the articles should appear *in print form* in time for distribution to the Legislature of Illinois, before its adjournment in the latter part of May. This agreement was fulfilled fairly well—a good part of the printing was sent on in good season, and proof pages of all the balance were used before the legislature, so that there was no ill-result due to the method of publication.

On the completion and shipment of the University of Illinois articles, the publication of Vol. IX was necessarily allowed to stand for six weeks, while the other accumulated duties, already much in arrears, were given attention. In July, after returning from the summer meeting, the work was again taken up and pushed steadily through the summer until September 4th, when the Secretary was again obliged to give publication up for a time, owing to the destruction of his home by fire, and necessary duties in consequence.

In the first week of October, the publication was again taken up, and was pushed to completion the first of November. The inordinately long time consumed was due to the great quantity of matter, the large amount and very particular character of some of the engraving required, and the inability of the Secretary to devote himself steadily to the duties of publication. The publication was edited by the Secretary alone this year, no editor or assistance being employed, and no fees or salaries being paid for anyone in connection with the publication.

Although the subject of publishing the Transactions has been discussed at every meeting of late years, and many suggestions have been made, with a view of reducing the burden of this work, nothing practical has yet been accomplished. The Secretary once more ventures to call attention to the fact that no hope of improvement exists until the Society is able to secure a secretary whose time can be paid for adequately, and whose sole or chief business must be that of advancing the interests of the Society. The truth of this proposition becomes clearer year by year, and the time is close at hand when the Society must find a means to secure and pay such a person, or else cease to grow and progress into the powerful organization which their years of hard work have brought within their grasp.

THE FINANCIAL STATEMENT.

The statement of the Society's financial condition is a complete trial balance from the books, and shows not only the actual receipts and expenditures for the year, but also the debits and credits.

DEBITS.

Brought forward from preceding year		$466.51
FROM DUES AND INITIATION FEES.		
215 associates @ $4.00	$860.00	
37 initiation fees @ $5.00	185.00	
1 associate dues @ $3.00	3.00	
6 associate dues, 1908-09, @ $4.00	24.00	
3 associate initiation fees, 1908-09, @ $5.00	15.00	
9 associate back dues, 1906 or prior, @ $4.00	36.00	
46 members @ $5.00	230.00	
6 members initiation fees @ $5.00	30.00	
		$1,383.00
FROM SALE OF PUBLICATIONS.		
17 Volume I	$20.90	
17 Volume II	38.40	
18 Volume III	28.40	
18 Volume IV	34.65	
16 Volume V	40.70	
20 Volume VI	44.20	
13 Volume VII	37.70	
1 Volume VII, Part 2	1.25	
28 Volume VIII	85.44	
32 Volume IX	108.29	
42 Manuals	41.01	
12 Branner Bibliographies	24.20	
10 Sets of Seger's Collected Writings @ $15.00	150.00	655.14
Total		$2,504.65

CREDITS.

Cost of publishing Volume IX—		
Stenographic report	$241.00	
Illustrations, Drawings and Engravings	322.21	
Printing, Binding and Casing	1012.77	
Copyright	1.00	
		$1,576.98
Cost of Collected Writings of Seger—		
Paid to Chemical Publishing Co. @ $11.67 per set, 10 sets		116.76
Cost of Running Secretary's Office—		
Secretary's Assistant	199.92	
Postage, Stationary and Supplies	36.63	
Insurance on Volumes of Transactions	10.00	
Freight and cartage	48.14	
Convention circulars, notices, and prospectus	57.15	
Telegram	.60	352.44
Travelling Expenses—		
Committee on co-operation between Federal and State Surveys and the Society on Clay Testing, Etc.	83.20	
S. G. Burt, Delegate, representing the Society to the dedication of the Carnegie Engineering Society Building at New York	50.00	133.20
Outstanding Accounts—		
Amount outstanding for dues	111.00	
Amount outstanding for Transactions	95.83	
Amount outstanding for Branner Bib.	6.20	213.03
Cash on hand	112.24	112.24
Total		$2,504.65

This statement is an exceedingly important one for the Society. For the first year in our history, we have to show a falling-off in our receipts. This, together with an increase in our expenditures, has well nigh wiped out our hitherto comfortable bank balance. The analysis of the cause of this situation is as follows:

Firstly. Volume IX was inordinately expensive. The stenographic report was not more costly than usual, but the illustration of the volume cost more than three times the usual previous expense. This could have been avoided in part. by putting many curves on one sheet instead of singly and otherwise condensing the presentation, but not without distinct loss of quality, and danger of obscuring the facts. The book as a whole is certainly not over-illustrated. The printing was at about the same rate

as has been paid before, but the large size of the book made the bill heavy. The total cost of Vol. IX is actually less per page (1576.98÷808= 1.95) than Vol. VIII (914.65÷411=2.22), but the aggregate is 72% greater than last year.

Secondly. The running expenses of the Society, for the Secretary's office, and for the handling of its business, is lower than before (353.44 in 1907 vs. 392.75 in 1906) by 39.31, so that no undue costs can be charged to this department.

Thirdly. There were some expenses this year of a kind not before incurred, in the travelling expenses of our President to New York to represent the Society at the dedication of the great Carnegie Engineering building, and the travelling expenses of the Committee on Co-operation, which were recommended by resolution of the Society at St. Louis, but these items together only amount to $133.20, or about what has been paid out for editorial work hitherto, and which was eliminated this year. The expenses therefore have not undergone any novel or dangerous expansion in kind or amount; there is only just such a fluctuation as we may always expect from year to year.

On the other hand, the revenues have fallen away in a manner which merits a careful study of the cause. The total shrinkage in receipts for the year amounts to $326.88, of which $300.38 is from reduction in sales of our transactions, and $26.50 represents shrinkage in the amount of money collected in the form of dues. It may be explained that the latter item, shrinkage in dues, represents failure to collect dues, rather than loss in membership. The list has actually increased by some twenty-five members, but there has been an increasing difficulty in collecting the dues, and there is now a larger delinquent list than a year ago. Monthly statements have been sent to all delinquents, and every reasonable effort excepting begging appeals from the Secretary has been made to collect the money. It seems probable, therefore, that we may lose a considerable number of these members, in spite of our efforts to keep them with us.

The shrinkage of $300 in our sales of publications is the most serious cause for reflection. Of this sum about $100 represents the early sales of the Branner Bibliography, but there were about twice as many sales of the Transactions in 1906-07 as in 1907-08. Inasmuch as no paid public advertising has ever been done, and as the sales represent only what can be gotten through the Secretary's correspondence, and by the efforts of members of the Society, it is apparent there has been a good deal less effort to sell the Transactions this year than heretofore. The Secretary is not conscious of any change in the administration of the affairs of his office, or any less effort to sell the Transactions by correspondence. It remains to be found whether the members of the Society have done their part in placing the work of the organization before the public.

Considering the situation from a more optimistic point of view, the facts show that the Society now has an income of from $1,800.00 to

$2,000.00 a year, and that the expense of printing a volume of transactions of about 600 pages will be from $1,200.00 to $1,400.00, and its administrative expenses on the present basis should not exceed $400, which will leave a sufficient margin to cover all ordinary emergencies.

We can, therefore, so far as can be seen or fairly be expected, continue to exist comfortably on the present scale, but we cannot expand or take any steps toward the higher field of usefulness which lies at our very threshold.

INCREASE OF DUES.

The Board of Trustees was requested by the Society at last year's meeting to consider the advisability of increasing the dues, as a means of increasing the revenue. They have done so, but after consideration, voted not to submit an amendment to the Constitution to the members at this election. The Board's reason for not taking action was the fear that an increase in dues might cause a decrease instead of an increase in revenue. The whole problem of increasing the revenue, in order to be able to undertake work on a more important scale, is before the Society and should be kept on the minds of the members until a way is found.

PUBLICATIONS.

An inventory of the publications has been taken and is shown in the following table:

	Remaining Feb. 1, 1907	Rec'd since	Sold since	Otherwise disposed of	Remaining Feb. 1, 1908
Volume I	262	*3	17	....	248
Volume II	250	*1	17	....	234
Volume III	257	*3	18	....	242
Volume IV	225	*1	18	....	208
Volume V	201	*2	16	....	187
Volume VI	230	*2	20	....	212
Volume VII	231	*1	13	....	219
Volume VIII	241	..	32	—1‡	208
Volume IX	...	498	270	—8‡	220
Manual Ceramic Calculation	139	...	42	....	97
Branner Bibliography	914	*108	12	—2†	910
Totals	2950	521	475	11	2985

*Miscount in former years.

§Vol. 8 one free copy, Vol. 9 eight free copies, to journals.

†Given to the Author, on request.

‡One extra bundle, not counted in last year's inventory.

The volumes are kept in a room devoted to the purpose and under the constant care of one person. They are kept insured in the sum of $2,000. Their value at an estimate of $3 each for the Transactions, $2 for the Branner Bibliography, and $1 for the Manual foots up to $7,851.00, showing that the Society has a very comfortable asset stored up in this form. In event of sudden and severe financial need, a considerable sum could probably be realized from their sale at a lower price than the present prevailing rate.

The year has passed away without any vigorous effort being made to place the Branner Bibliography on the market. What is needed is an active business campaign, including advertising, correspondence and energy. These requirements seem simple, and there would appear no reason why it could not have been accomplished, but the fact remains that the editorial work of the Secretary has been so heavy for the current year. At no time has there been an opportunity for the Secretary to take up the additional labor of undertaking the sale of this publication. The longer the matter is deferred, the more difficult will it be to sell the volume, and it is hoped that some method of handling the matter may be agreed upon at this meeting.

The sales of the Collected Writings of Seger still continue, though in somewhat diminished volume; there has been a profit of about $35 from this source for the current year. It is certainly remarkable that the Society has succeeded in selling so large a number of volumes of this high priced work, with a cheaper and incomplete edition on the market. Without doubt, the sale will still continue for some years, but it is not likely that the Society will derive any important revenue from it.

The sale of the Manual of Ceramic Calculations is the one publication which has shown an increase this year. At the present rate, the issue will be exhausted in two more years. The Society has reason to congratulate itself on this piece of business. It was the pioneer publication of its kind. Since it was published, there have been two excellent publications brought out, one by Jackson in England and one by Pukall, of Germany. It hardly seems probable that it will pay the Society to publish another edition, certainly not without considerable modification and the incorporation of a number of subjects not touched upon in the first.

INDEX.

With the publication of Volume X, the total publications of the Society, exclusive of Seger and Branner, will amount to approximately 4000 pages. None of the volumes are indexed at all, and now that our literature is beginning to be seriously sought and used by the world, the need of an index is increasingly felt. The index should be general—not confined to an author index, nor to a subject exclusively, but to include both. An index of fair quality, without going into too close an analysis of the subjects, would run from 200 to 300 pages. It could probably be prepared for $100.00 to $150.00, ready for printing.

BINDING THE VOLUMES.

The large size of Volume IX, and the impossibility of putting up a volume of this size adequately or neatly in paper covers, and the difficulty in even delivering the volumes in good condition, make it necessary to bring up this ever recurring subject again. The cost of binding will vary from 15 to 25 cents per volume, and will make our literature far more durable and satisfactory. The increase in cost will not cut seriously into the profits of the sales on each volume.

GROWTH IN MEMBERSHIP.

The growth in membership has continued good during the current year. Beginning the year with a total of 231 members on our rolls there are at the present time 256, a net gain of 25 members, or 10.8%. The percentage gain is less than that of the year preceding, inasmuch as it is computed on a larger number of persons. There is, however, a somewhat smaller list of new associate members elected than in the year preceding. The number of full members has grown steadily, but very slowly. The percentage of full members to the total is 18.3%, a few tenths of a percent higher than last year.

The present status of our rolls is as follows:

Brought forward February 1st, 1907—	
Honorary members	2
Full members, resident	40
Full members, foreign	1
Associate members, resident	168
Associate members, foreign	20
Total	231
Accessions	
By election to full membership	6
By election to associate membership	35
Total gain	41
Losses	
By death, associate members	2
By resignation, associate members	3
By promotion to full membership	6
By failure to pay dues	5
Total losses	16
Net gain	25

Present Status, February 1st, 1908

Honorary members	2
Full members, resident	46
Full members, foreign	1
Associate members, resident	185
Associate members, foreign	22
Total strength	256

To enable the Society to show a continuous and increasing growth, it will be necessary that the members undertake with increasing activity the duties of acquainting the public with our work, and inspiring them with a desire to be recognized among our membership.

REPORT OF THE COMMITTEE ON CO OPERATION

Between Federal and State Geological Surveys and the Society in the Matter of Research in Ceramic Lines.

The work of this committee has appeared in Volume IX, and also in the form of a reprint, which has been sent to the State Geologist in every state of the Union, and to many officials of the U. S. Geological Survey, and a considerable number of working geologists in the various universities in the country. Without doubt, the advice of the Committee will at least influence the action of State Geologists in many cases in the future where clay reports are to be undertaken. The expected entrance of the U. S. Geological Survey into this field of work did not materialize; owing to a change in the division of funds for the U. S. Geological Survey for the last year, it was impossible for them to open up any new department, or even properly support some departments already in existence. The project is not forgotten, however, and if some of the legislation now before Congress is enacted into a law either creating a Bureau of Mines, or creating a permanent Department for Technical or Engineering research, working in the Geological Survey, it is highly likely that the establishment of a ceramic experimental station will be given consideration. Meanwhile, the Society may properly feel that its main objects have been achieved, in the fact that those in authority recognize more clearly the need of the work, and the propriety of this organization influencing the character of the work to be undertaken.

SUMMER MEETING.

The question of a summer meeting is still open. In many respects, the present performance is unsatisfactory, and yet the results which it brings are too promising to justify dropping it. On the last occasion, which was in many respects the best arranged and most carefully managed one in recent years, the attendance was at first very small, though many

joined the party on the last day. Those who take these trips, enjoy and profit from them very greatly, but in one way, the Society is not much strengthened by holding public gatherings in which so small a number take part. It would seem that the summer trip should not be abandoned, as it fulfils a purpose not attainable during the winter meeting. It would also seem that the results of the recent year's meetings have not been commensurate with the expenditure of labor and energy in organizing and managing them. The policy involved in this matter should receive consideration at the hands of the Society.

OUTLOOK.

The Society enters at this meeting upon its second decade of existance. The conditions are very different from those of ten years ago. Beginning as an experiment, with a very small following, and without any wide recognition of the need of such an organization, the Society has increased slowly but steadily; has built up a solid and well-knit organization; has published much valuable literature; has sharpened the spirit of investigation in our still little-known field of science; has broadened the point of view alike of manufacturer and worker; has beaten down the barriers of the old-time trade secrecy, and best of all has opened the doors of our minds to the joys of giving and the pleasures of brotherly co-operation.

While we enter upon our work now with the advantages of these things in our favor, we also have correspondingly heavier responsibilities. To maintain ourselves on the plane of the present, and make each year show a still higher range of achievement in the quality of our work is more difficult now, by far, than it was a decade ago, but it is the task to which we must now address ourselves.

For the Board of Trustees,

Edward Orton, Jr.,

Secretary.

TREASURER'S REPORT

Columbus, O., Feb. 3, 1908.

Members and Associates of the American Ceramic Society:

Your treasurer's statement is as follows:

RECEIPTS.

To balance last report	$292.46	
To March collections by secretary	469.10	
To April collections by secretary	551.29	
To May collections by secretary	216.21	
To June collections by secretary	157.83	
To July collections by secretary	88.70	
To August collections by secretary	72.55	
To September collections by secretary	37.10	
To October collections by secretary	66.36	
To November collections by secretary	111.50	
To December collections by secretary	22.63	
To January collections by secretary	218.00	$2,303.73

EXPENDITURES.

By vouchers attached	$2,155.55	
By money orders returned to secretary	12.00	
By vouchers issued but not presented to bank for payment:		
M. L. Seymour	16.66	
Chem. Publishing Co	5.32	
Adams Express Co	1.85	
By error in money order per receipt attached	.11	$2,191.49
Balance		$112.24
Balance per bank book attached	$136.07	
Vouchers issued but not presented for payment as above	23.83	
Actual balance	$112.24	

Also attached is voucher for $19.48 which was issued prior to date of last report but had not been presented for payment.

Respectfully submitted,

ELLIS LOVEJOY, *Treasurer.*

Examined and found correct, February 4, 1908.

ERNEST MAYER,
W. A. HULL,
A. R. CAMPBELL,
Auditing Committee.

RULES

OBJECTS.

The objects of the American Ceramic Society are to promote the arts and sciences connected with Ceramics by means of meetings for social intercourse, for the reading and discussion of professional papers, and for the publication of professional literature.

MEMBERSHIP.

The Society shall consist of Honorary Members, Members and Associates.

Honorary Members must be persons of acknowledged professional eminence, and shall not exceed five in number.

Members shall be persons competent to fill responsible positions in Ceramics and have suitable qualifications.

Associates shall include persons interested in Ceramics and the allied arts.

Honorary Members shall be proposed by at least five members, approved by the Board of Trustees, and receive at least 90 per cent. of the votes cast by letter ballot at the annual meeting.

Members and Associates shall be proposed by at least three Members or Associates, approved by the Board of Trustees, and receive at least 75 per cent. of the votes cast by letter ballot. A candidate for admission must make application on a form prepared by the Board of Trustees which shall contain a written statement of his age, professional experience, and that he will, if elected, conform to the laws, rules, and requirements of the Society.

All Honorary Members, Members and Associates shall be equally entitled to the privileges of membership, except that only Members shall be entitled to hold office and to vote. Applicants for a change in grade of membership shall conform to the requirements of a new applicant.

Any person can be stricken from the membership of the Society on the request of five or more members, on the recommendation of a majority of the Board of Trustees, if he fails to resign on the advice of the Board of Trustees. Such person, however, shall be first notified of the charges against him, and be given a reasonable time to appear before the Board of Trustees, or present written defense, before final action is taken by the Board of Trustees.

DUES.

Honorary Members shall be exempt from all dues.

The initiation fee of Members shall be ten dollars, and of Associates five dollars, which if not paid within six months after election, will render the election void.

The annual dues for Members shall be fixed by the Board of Trustees, but shall not exceed five dollars per year.

The annual dues for Associates will be fixed by the Board of Trustees, but shall not exceed four dollars per year.

Any Member or Associate in arrears for over one year may be suspended from membership by the Board of Trustees until such arrears are paid.

OFFICERS.

The affairs of the Society shall be managed by the Board of Trustees, consisting of a President, Vice President, Secretary, Treasurer, and three Trustees, who shall be elected from the members at the annual meeting, and hold office until the adjournment of the meeting at which their successors are elected.

The President, Vice President, Secretary and Treasurer shall be elected for one year, and the Trustees for three years; and no President, Vice President, or Trustee shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually appertain to their offices, or may be delegated to them by the Board of Trustees or the Society; and the Board of Trustees may at its discretion require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Board of Trustees, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officer to execute his duties within a reasonable time, the Board of Trustees, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum; but the Board of Trustees shall be permitted to carry on such business as it may desire by letter.

ELECTIONS.

At the annual meeting, a nominating committee of five Members, not officers of the Society, shall be appointed, and this committee shall send the names of the nominees to the Secretary at least 60 days before the annual meeting, who shall immediately forward the same to the Members. Any other five members may also present the names of any candidates to the Secretary, provided it is done at least 30 days before the annual meeting. The names of all candidates, provided their assent

has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or an independent nominating committee, which shall be mailed to every member, not in arrears, at least 20 days before the annual meeting. The ballot shall be enclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary for collection. The blank envelopes shall be opened by three Scrutineers appointed by the Chair at the annual meeting, who will report the result of the election. A plurality of the votes cast shall elect.

MEETINGS.

The annual meetings shall taks place on the first Monday in February, at such place as the Board of Trustees may decide, at which time reports shall be made by the Board of Trustees, Treasurer, and Scrutineers of election, and the accounts of the Treasurer audited by a committee of three appointed by the Chair.

Other meetings may be held at such times and places during the year as the Board of Trustees may decide, but at least 20 days' notice shall be given of such meetings.

Seven members shall constitute a quorum at any regular meeting, and a majority shall rule, except where otherwise specified.

The order of business at the annual meeting shall be:—

1. Reading of Minutes of last meeting.
2. Reports of the Board of Trustees and Treasurer of the Society.
3. Announcement of Election of Members.
4. Announcement of Election of Officers.
5. Appointment of Nominating Committee.
6. Old Business.
7. New Business.
8. Reading of Papers.

PUBLICATIONS.

The Board of Trustees shall act as a Publication Committee, and decide as to what to publish. The publications of the Society shall be sent to all Members and Associates not in arrears. The Secretary will furnish each author with reprints of his papers at cost price, provided due notice is given that reprints are desired.

The Society is not, as a body, responsible for the statements or opinions expressed in its publications.

PARLIAMENTARY STANDARD.

Roberts' "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

AMENDMENTS.

These rules may be amended at any regular meeting by a two-thirds vote of a letter ballot at the subsequent annual meeting, provided a written notice of such proposed change is sent to each member at least 30 days before said annual meeting. Said proposed amendments shall be printed on the balolt for officers and counted by the same Scrutineers.

PUBLICATIONS.

The publications of the Society are as follows:

DESCRIPTION OF VOLUME.	Price to members.	Price to Others'
Vol. I. Transactions for 1899, 110 pages, bound in paper,	$0.50	$4.00
Vol. II. Transactions for 1900, 278 pages, bound in paper,	2.00	4.00
Vol. III. Transactions for 1901, 230 pages, bound in paper,	1.00	4.00
Vol. IV. Transactions for 1902, 300 pages, bound in paper,	1.50	4.00
Vol. V. Transactions for 1903, 420 pages, bound in paper,	2.50	4.00
Vol. VI. Transactions for 1904. 278 pages, bound in paper,	1.50	4.00
Vol. VII. Transactions for 1905, 454 pages, bound in paper,	2.25	4.00
Vol. VIII. Transactions for 1906, 411 pages, bound in paper,	2.00	4.00
Vol. IX. Transactions for 1907, 808 pages, bound in paper,	3.00	4.00
Manual of Ceramic Calculation (contained in Vol. II as a part thereof,) 86 pages, bound in paper,	1.00	1.00
The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (A) Treatises of a general scientific nature, (B) Essays relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages, 552. Bound in cloth.	7.50	7.50
The Collected Writings of Dr. Hermann August Seger, Volume II. Contains (B) Essays on Whiteware and Porcelain. (C) Travels, Letters and Polemics. (D) Uncompleted works, and extracts from the archives of the Royal Porcelain Factory. Pages, 605. Bound in cloth.	7.50	7.50
A Bibliography of Clays and the Ceramic Arts, by Dr. John C. Branner, 1906, 451 pages. Bound in cloth. Contains 6027 titles of works on Ceramic subjects.	2.00	2.00
Cost of full set, not including manual.....	$34.25	$53.00

At the Cincinnati meeting, the Board of Trustees fixed a sliding scale of prices to apply to the sale of volumes of the Transactions, when the number unsold falls below 200 copies. As the copies become scarcer, prices will be increased to both members and others. The supply of one of the volumes has already fallen below 200 copies, and others will probably pass below this mark during the coming year. Members and Associates who do not yet own full sets are advised to procure them at once.

At the same meeting the following resolution was adopted:

Resolved, that the custom by which members and associates may obtain copies of the Transactions at reduced or so-called "members' rates," is intended only to enable each person to obtain one complete file of the transactions.

The necessity for this resolution arose from the expressed desire of a member to buy a copy of the transactions, with the intent to sell it to a friend for whom he wished to save the additional price charged to non-members. In accordance with the spirit of this resolution the Secretary will not supply more than one copy of a volume to a member at reduced rate, except when loss or destruction of a volume gives good cause for so doing.

Every member or associate receives one copy of the Transactions free for each year for which he pays dues. He is entitled to purchase copies for the years antedating his connection with the Society at the costs indicated in the first column. All others can obtain copies at the prices listed in the second column by sending order, accompanied with check, to

EDWARD ORTON, JR.,
Secretary.

Columbus, Ohio.

PAPERS AND DISCUSSIONS.

ADDRESS OF THE RETIRING PRESIDENT.

BY

STANLEY G. BURT, Cincinnati, Ohio.

It seems hard to realize that we have gathered for our 10th Annual Meeting, and it is equally hard to realize how successful these past ten years have been. I doubt whether the most sanguine of our founders would have dared prophesy that at this time we would have so successful a past to look back upon. Have we not reached a point at which we may well pause and briefly review our past and then look forward to our future?

In 1898 a few enthusiasts decided the time had come to organize a society whose objects should be "to promote the arts and sciences connected with ceramics by means of meeting for social intercourse, for the reading and discussion of professional papers, and for the publication of professional literature." It was the aim of these men to advance the clay industries by three methods: first, by social intercourse, second by reading professional papers and third by publications. Now, how have we succeeded in these three aims?

Social intercourse is very justly placed first. Last spring your society was honored by an invitation to send a representative to the dedication of the United Engineering Societies' Building. In this country we have three great leading societies of engineers,—the Mechanical Engineers, the Mining Engineers, and the Electrical Engineers. These three societies were maintaining separate offices in New York City. Through the generosity of Andrew Carnegie, who gave ($1,000,000) one million dollars, a most magnificent building has been built in which these societies are now united. While Mr. Carnegie's gift paid for the building, the three founder societies paid for the lot. The

top floor is devoted to a combined library; beneath this each of the founder societies has an entire floor for office purposes. Provision is made on lower floors for other engineering societies, while the entire second and third floor is given up to a beautiful auditorium. Should we at some future time hold our business session in New York I have no doubt that suitable rooms could be obtained in the building.

It was to the dedication of this home of the engineer that you were invited to send a representative. Your board of trustees decided that this honor and pleasure should fall to my lot. I would gladly describe to you at length that memorable meeting. Practically every prominent technical society and school in the world was represented. Many able addresses were made, but of all these to me the most able was that of Mr. Carnegie.

The keynote of his address was strength in unity. How had it been possible for the American Engineer to so far surpass his foreign brethren? Simply because he was ready at all times and to the utmost of his ability to help his brother engineer. No secrecy or petty jealousy, but frank, open-hearted, true fraternalism. No great advance or achievement can be made without co-operation of many minds. 'Tis only with a thorough understanding of the work others have done that we are able, with its aid, to advance. The man so constituted mentally that he fears his brother worker, merely wants to rob him; or the one who wishes to receive but never to give has a mind so small it will always be an impossibility for him to attain any great success. To further this all-important co-operation not only should the members of the separate societies meet, but Mr. Carnegie felt that if the various societies could be brought together under one roof, great gain must result to all. This has been accomplished in this new building.

If now it be true that the secret of our national success has been this free exchange of ideas, how best can it be fostered? By social intercourse. 'Tis the true heart to heart talk that has done those of us who have attended our

meetings more good than all our papers or publications put together. That our society during the past ten years has been able to gather together in social intercourse so many men who fully realize the value of mutual aid, who have come ready to give as well as to receive,—this to me seems our greatest achievement.

The second object of the society was the reading and discussion of professional papers. If I had here to show you Volume I in one hand and Volume IX in the other, no comment would be at all necessary. We have had more papers offered at each meeting and they have been more and more valuable. While our able secretary has urged us all to contribute, and we ought to do so, it is nevertheless true that he has been wholly unable to have read all the papers that were offered.

The third object of our society was the publication of professional literature. Under this head our nine volumes of transactions naturally come first. I have already mentioned their gratifying growth in size and quality. We have also translated and published the Collected Writings of Dr. Seger. Had we accomplished nothing else we might justly feel that the society had not been organized in vain. Then we published our Manual of Ceramic Calculations. This little book is so clearly and admirably written that it can be readily understood by all, and has deservedly become a text book in our ceramic schools. Our most recent publication was the Branner Bibliography, of which we are justly proud. These three works are true labors of love, for the translators of Seger, the authors of the Manual and Dr. Branner himself never received one cent for the hard work done. The Seger translation and the Manual have paid back all costs, and give us in addition a very helpful annual income. I trust the same will be true of the Bibliography when it has had time to be properly distributed.

Before leaving the consideration of our past history there is one more point about which I think we may all feel satisfaction,—and that is that while accomplishing

all this good work we at the same time kept a balance in the treasurer's hands and had no debts. The past year has been one of unusually heavy expense, but I feel sure the society has met all of its obligations and has a balance to its credit.

In turning now to consider our future, under the same three heads, first comes our future social intercourse. Our recent meetings have furnished our secretary with so many papers to be read that he has felt compelled to give the evenings to business sessions at which papers could be read. Personally I feel this is a mistake, because in a large measure it puts an end to our social intercourse, which to my mind is the greatest good the society can accomplish. In our early years what Prof. Wheeler called our "section Q" was to the individual member the most valuable part of our meetings. After a hard day's work with our professional papers we gathered informally in some comfortable spot and did our best to help each other with the thousand and one problems that trouble each and every one of us. We have labored together until two o'clock in the morning and been sorry to stop then. This type of social intercourse does not mean going to the theatre or any such performance, but it means that congenial souls, having similar tastes and aspirations, and working perhaps along parallel lines, will get together to talk over the struggles and accomplishments of the year, the successes and failures, the pleasures and disappointments, and that each will receive help and encouragement and inspiration for renewed exertions. At our recent meetings we have our long morning and afternoon session followed by an equally long evening session, after which we are glad to sleep. Now I do not believe any human being can follow our speakers and fully absorb their papers during such a long period. Then again the scope of our program is so broad that necessarily we can not have the same keen interest in all subjects offered. Those of us who are potters for instance have but a broad general interest in the sand-lime brick or cement industry,

and of course the reverse is equally true, the cement man cares little about the terra cotta kiln.

I believe our future meetings should give us certain sessions devoted to topics of general interest to all, then sessions devoted to specialties interesting to a more limited number. When this can be done then the social side can also be arranged for in this manner. Our secretary always calls for subjects we would like to have discussed. They are almost always of the special class, and really call for an informal treatment, so are not best treated in a formal session. What we want is a discussion, if it takes all night, and we don't want to be stopped just as we get fully interested by the chair announcing that no more time can be allowed to that subject, as the regular program is being delayed. I would suggest that assuming we have had our official morning and afternoon session of general interest the program would state that an evening official session would be held on some special subject, and that one or more section Qs would be held informally at the same time, with the man who wanted a subject discussed as chairman. The members would then be left the choice either to attend the official session, or to join one of the informal section Qs. The objections to this plan I suggest are first that it might draw too many members from the official evening session. Answering this I would say that if it did do this 'twould merely prove that it was best to abandon business sessions in the evening. A second objection is much stronger, which is that all discussion out of the official session is lost to the society, as no record could be kept of it. This is true, but I feel that the discussions I am endeavoring to call forth are ones that the society by our present method can not get, nor the individual member either, as these heart to heart talks have largely ceased to exist. The great argument in favor of this plan for furthering our social intercourse is that we have lots of valuable latent material that is lost and can only be reached in this way. The drift of our professional papers has been toward a higher and higher standard of excellency. Our subjects are now

treated with such exhaustive research that it seems actually at times absurd to attempt to discuss or criticise off-hand such careful work. Your trustees have long realized this and I have hoped, as a solution, that we would be able to print our best papers and distribute them for study some time before the meeting is called. No one could be more delighted than I am that our papers have shown such a splendid advance, and I recognize fully that unless we hold our standard high and keep raising it higher the actual life of the society would be endangered, but in striving for this end we will make a great mistake if we sacrifice all other aims. The type of paper we are striving for is becoming more and more one that can only be prepared by those fortunate few who have all the facilities, both of time and means, furnished by life at a university or school; they may well be called scholastic papers.

The man bound to a factory has both his time and facilities limited and cannot prepare such a paper, no matter how valuable the material he has gathered. Worse than this he feels that because he cannot show some elaborate series of trials he'd better keep still altogether. While I spoke of a university furnishing facilities which a factory does not, when we wish to pass out of theories and trials into actual practice, then the factory has the only facilities. So all theory and trials must be tested by practice, and it is reports of these practical factory tests, on a large scale, of our theories, that I feel we are not getting enough of and ought to encourage. The man who has made this practical test is almost always one who has been too busy or is too modest to even think of writing a paper. He ought to be encouraged to do so, and I claim no better training can be given him than a social session, where he can discuss freely with his brother workers his daily problems, what he has observed in his practice, where theories have proved true and where they have broken down.

When one of our best railroads planned to use electricity for steam, expert engineers calculated and prepared

for every danger they could forsee. The train was started, struck a curve, and off it went in a terrible smash. Why? Was it mere carelessness? No. In calculating the engineers had failed to realize and properly allow for the difference between a steam and an electric locomotive, in that the center of gravity of the electric being lower it gave a far greater side thrust. So in our own work. Our theories may be right as far as they go, but it is only by a practical test that we can be certain that some hidden factor has not been neglected.

Some years ago I made the suggestion that members be encouraged to bring samples of their good or bad results to the meeting. 'Tis true that many of our papers have been illustrated with admirable samples, but I mean the man who merely has trouble and not a paper. Let him bring samples of his trouble, then in a semi-private discussion he may gain light which will enable him to cure his trouble and at the same time prepare him to give us a paper at our next meeting. In a measure we have encouraged him to do this in the official session, but he has come to feel, and I think justly, that there will be no time for him with our present crowded programs. Then again, the skeleton in the closet dreads to step out into the full lime light. It needs to be coaxed out, and it is only a social session that can furnish the necessary encouragement. It even takes courage at times to confess to our intimate friends some of our really serious troubles. Our summer meetings have furnished a splendid chance for just such social intercourse as I have been describing, and I trust we may continue to have those delightful outings. The great trouble with the summer meeting is that only a few of our members have been able to avail themselves of its pleasures, and it is most often the busy practical man I've been speaking of who is unable to attend. I feel too that of late years even our summer meetings have grown too strenuous. Our kind hosts have prepared too much for us, so that again we have the crowded program.

The point I wish to make is that the future of our professional papers seems assured, as each succeeding meeting has shown them growing in number and quality, but the future of our social intercourse demands your earnest attention. While it is imperative that our papers be good to have our meetings attended, it is equally true that our members will not come at the great sacrifice always involved merely to hear some long scientific papers read. It is the meeting of old friends for social intercourse, of the kind I have always described, which really constitutes the greatest attraction of our meeting.

Some may argue that if any members desire this social intercourse, they will provide for it themselves, and that there is no need of its official recognition by the society. The objections to this are first, as long as the official program offers at all sessions papers of general interest we feel we ought not to lose them, so often are compelled to attend an entire session to be sure of hearing some one paper. In the second place under the present plan it is the duty of all members to attend for the general good. The most important objection, however, to the Society's failing to officially recognize this social intercourse, is that while here and there old friends may get together quietly, *sub rosa* as it were, as no general invitation or encouragement has been extended or can be extended, the younger, that is, newer member, is apt to be left out altogether.

One of the foundation principles of our society is charity. Let us publish to the world the knowledge we have gained and do our best to help our fellow workers. Why then should we not let this charity extend to our fellow members of this society in the fullest measure possible?

Now as to the future of our publications, other than transactions. With the success of our past publications in view we should feel encouraged to publish such works as our board of trustees may deem worthy. I trust the day may come when a volume written by some member will be

published by the society just as the Manual and Bibliography were.

I have served you officially through nine of the ten years of the society's existence, and I thank you for the honor and for the universal kindness shown me, and I assure you that I retire with the same enthusiasm and same desire to aid the society in any way possible that I felt ten years ago.

A CONVENIENT CARBON RESISTANCE FURNACE.

BY

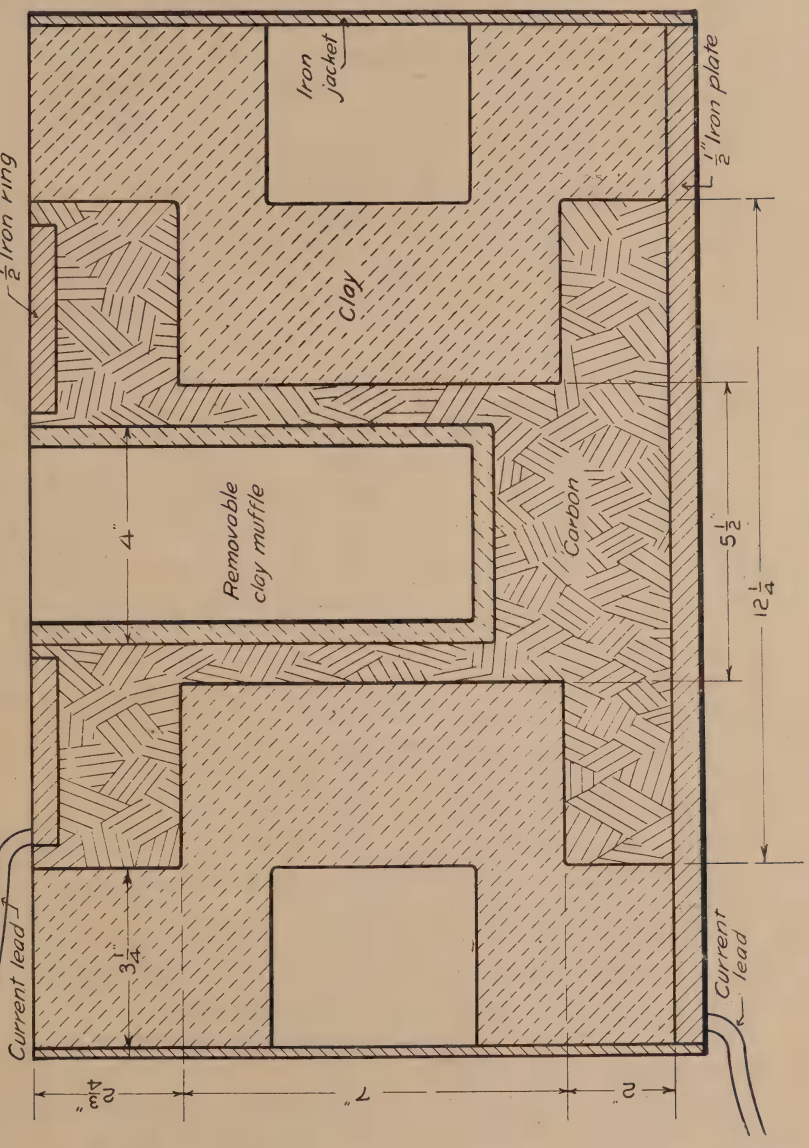
*A. Coggeshall and A. V. Bleininger, Columbus, Ohio.

The carbon resistance furnace offers no more interesting problem from the point of view of ceramics, than from the electrical standpoint. Here the difficulty is in obtaining proper regulation. For ease of manipulation in regulation, alternating currents seem to offer advantages not possible with direct currents. This alone would be a strong argument for the use of the former, and besides this the alternating currents render the starting of the heating process simple, while it is troublesome and sometimes expensive with direct currents.

In the first place, the furnace requires for successful operation a considerable range of voltages. Let us suppose that there is available for running the furnace a constant source of electromotive force from supply mains of some sort. At the start, the voltage applied to the furnace must be relatively high, and be gradually reduced as the carbon is heated up. But after the temperature has mounted a few hundred degrees, the voltage must be increased in order that the heating may continue at a uniform rate. To operate the furnace from ordinary room temperatures to temperatures of 1400° to 1500° C will require, perhaps, a variation of voltage across the furnace terminals of 30 or 40% either above or below the voltage necessary for starting. To obtain this variation with direct currents, would require the insertion in the circuit of resistances which could be varied from time to time, provided there were no direct means of adjusting the supply voltage, as would often be the case. This would mean power wasted in the

*This paper, read at the St. Louis Meeting, was sent to Mr. Coggeshall for revision and was not returned in time for publication in Vol. IX.

TRANS AM. CER SOC VOL. IX COGGESHALL AND BLEININGER, PL. I

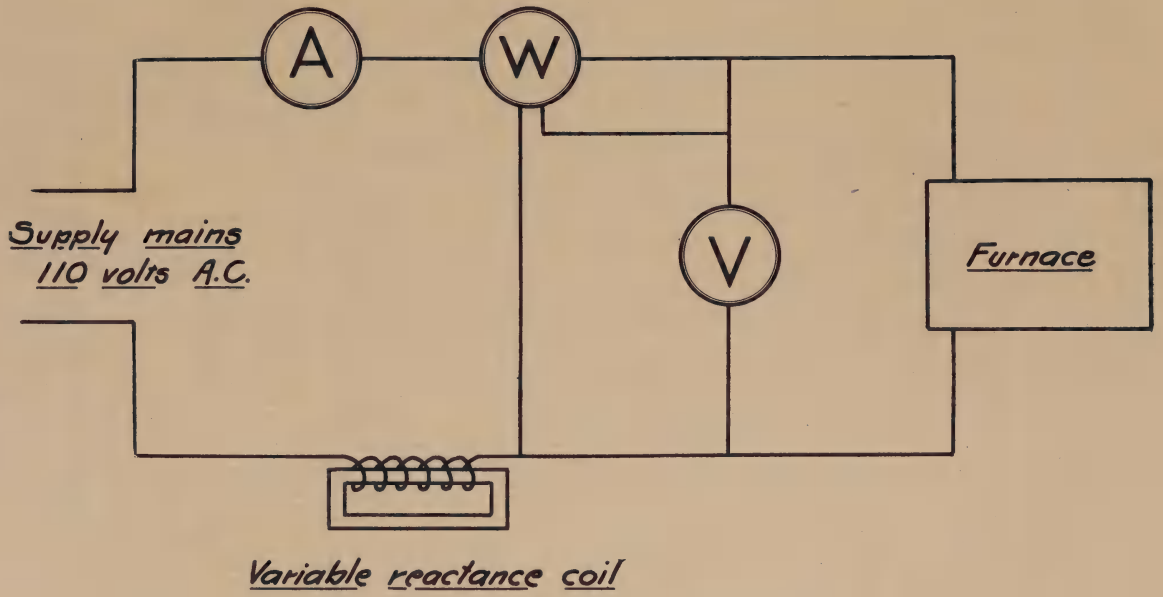


I^2R of the series resistance, and constant adjustment of the resistance necessary to provide the proper voltage.

With alternating currents, however, this adjustment of voltage may be obtained without the expenditure of power, and through quite as wide a range, and may be made more nearly automatic.

Investigation into the phenomenon of change of resistance of the carbon mass, reveals the fact that the change is a very uncertain quantity, depending quite as much on the manner in which the power is applied to the circuit, as upon the density of the carbon, the temperature of the furnace, and the manner in which connection is made to the carbon particles, and the shape and heat insulation of the receptacle. It is found to be well nigh impossible to duplicate the resistance changes of any one run, and especially so if the voltage is applied in a haphazard fashion by manual adjustment. It is therefore desirable to secure a method of operation which will be equally efficient, no matter what the state of the furnace, nor what its resistance may be at the time it is required to start operation. The method of regulation should be such that no matter what the value of the resistance, the voltage will automatically adjust itself to the proper value, the instant the circuit is closed. These are the conditions to be observed, if the furnace is to be operated most efficiently and uniformly, with the least possible use of power.

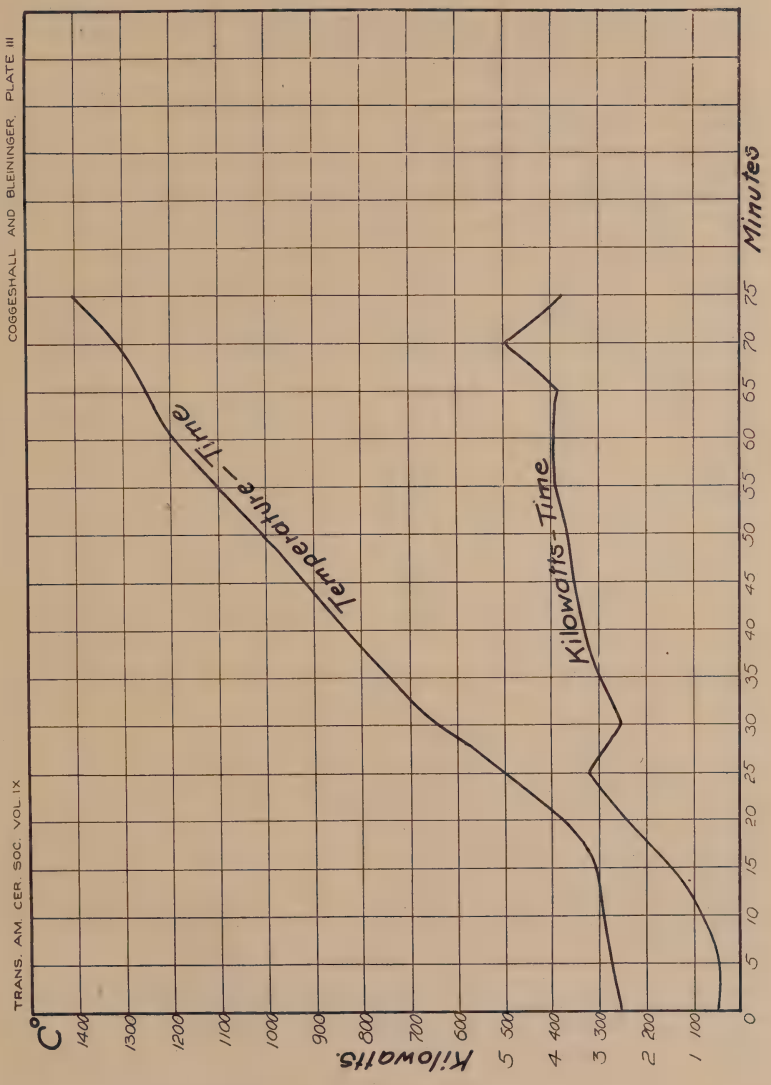
The one characteristic change that seems always to repeat itself in the resistance variation of the carbon, is the rapid decrease in resistance when the circuit is first closed through the cold furnace. The freeing of the gases contained by the carbon particles is very vigorous and rapid at this early stage, and this presses the particles more tightly together as they slowly heat up, and thus reduces the resistance of the mass. When this initial stage has been passed over, and the gases freed, the resistance becomes more constant, and, as the rate of application of power becomes less rapid, will increase in value. It is when the resistance shows a tendency to increase that the


A
W
V
Supply mains
110 volts A.C.
Furnace
Variable reactance coil

voltage must be raised, for it is then that the carbon is in the act of cooling, and if the heating is to continue at a uniform rate, the energy supplied must be increased. In other words, the energy supplied electrically must be in excess of the heat losses of the carbon, and as the temperature increases, these losses become more nearly the equivalent of the energy that has been supplied up to that point. Therefore, if it is desired to carry the heating further, it becomes necessary to increase the voltage, and consequently the power that is supplied to the furnace.

This adjustment of voltage is obtained in the following manner: In series with the furnace, is placed an inductance coil, which consists of a few turns of copper wire, mounted on a closed magnetic circuit. The magnetic circuit is so arraged that for small currents, the inductance of the coil, and hence the choking action on the current, will be great, and will increase as the current increases. And as the current at the start is small, this still allows a high voltage at the furnace terminals. But as the current increases, due to a lowering of the resistance of the carbon, beyond a certain value, the choking action of the coil diminishes. In other words, the change in the choking action of the coil is just the reverse of the change in resistance of the carbon mass of the furnace. This provides the adjustment of voltage necessary to carry the furnace over the early stage of heating, and when demand for still higher voltages is made, to carry the heating further, the inductance of the coil must be cut down. This may be done gradually, and as needed, by varying the magnetic circuit's reluctance. The entire adjustment is thus obtained at the small expenditure of power necessary to overcome the magnetization losses of the iron core, and these are neglible compared with the I^2R of the furnace.

That the proper rate of increase of power may be obtained with this means of adjustment, is shown by the curves of power and temperature against time on the curve sheet. The curves are not as smooth as could be desired, and show that not quite the proper adjustments were made.


TRANS. AM. CER. SOC. VOL. IX
COGGESHALL AND BLEININGER. PLATE III
C°
Kilowatts.
Minutes
Temperature – Time
Kilowatts – Time

The total power expended for the case shown, for a maximum temperature of 1400 was 3.7 kilowatt hours. Another run showed a power expenditure of 3.8 kilowatt hours for a maximum temperature of 1300, and still another run showed that 10 kilowatt hours were necessary for a temperature of 1800° Cent.

The weight of the furnace, without the carbon, is 117 pounds and the weight of the carbon necessary is 15 lbs. There is a slight wasting away of the carbon when operating at high temperatures, and it is therefore necessary to supply new carbon from time to time. This can best be done by first compressing the carbon in the furnace by tamping with an iron and then filling up with new material.

NEW CRYSTALLINE GLAZES.

BY

J. Koerner, Ph. D., Coburg, Germany.

[Dr. Zimmer:—Among the ceramic studies of the past ten years the crystalline glazes have absorbed a good deal of interest, which is easily understood when we consider the importance of crystallization in our modern chemistry. It is to be hoped that, as crystallization out of liquid solution became a medium to advance our chemical knowledge, the crystals out of the solid solution of a glaze, formed at high temperature will become a welcome help to scientific ceramics. Therefore scientific ceramists on both continents have paid close attention to crystalline glazes, although their commercial value is very little, if any at all, and they may appear to the ignorant layman as mere ceramic curiosities. As was stated in the very interesting paper of Messrs. Purdy and Krehbiel at last years' meeting (Transactions, Volume IX, page 319) we have only very scattered literature on the subject, but I am very proud to state that the most valuable and complete records are to be found in the Transactions of our society (conf. Transact. Am. Cer. Soc., Vol. IV, page 37; Vol. V, page 50; Vol. VI, page 186; Vol. VII, page 42; Vol. VIII, page 336; Vol. IX, pages 319 and 782.) It is too early yet to deduce any laws from the result of those few researches, but every new experiment will be a step further, and I trust that the assembly will excuse me if I now read a paper given to me by Dr. Koerner, my successor as editor of the Sprechsaal, and former manager of the Majolika Works of Emperor William at Cadinen, instead of giving you an extemporaneous talk on American versus Continental Pottery, which may be better referred to the inofficial section Q.]

During experiments with uranium oxide in order to obtain a red color, which I started in 1896 and after an

intermission continued at the Versuchsanstalt of the Royal Porzellanmanufactur Charlottenburg during the year 1901-1902, I observed, that combined with lead, uranium oxide has a great inclination to form an aventurine-like glass. At first I attributed this phenomenon to the use of fluxes containing a high percentage of lead and tried to overcome the difficulty by applying fluxes high in alkalies, without however a satisfactory result. Finally I proceeded to substitute the lead-fluxes by bismuth and at once I obtained crystals of quite a peculiar formation, which appeared red, if looked at from above, but glittered like gold from the side and were imbedded in glaze of a nice yellow color.*

I had used at first a lead-uranium compound corresponding to the formula $PbO \cdot 2\ UO_3$; afterwards one of the composition $3\ PbO \cdot 2\ UO_3$. Although I obtained with these a red color, if proper fluxes were applied, the result was mostly a red surface filled with flitters, as said before, on the style of aventurine, but no crystals; even if up to 30% were added to lead glazes, the result remained the same and there appeared no crystals until I constructed lead glazes with additional bismuth oxide. These crystals, however, could not be compared with the well-known zinc and titanium crystals in regard to size, although they were interesting and effective on account of their peculiar color.

As it is a known fact that basic glazes with a high percentage of lead may segregate lead under certain conditions, which process will also lend a peculiar appearance to the glaze, I started to investigate whether the crystalline segregation might be caused by the lead or not. I tried at first glazes without lead, but containing bismuth, which showed the same segregation. However, the lead-uranium compound itself contained about 54% PbO, and hence I proceeded to construct a compound of the formula $Bi_2O_3 \cdot 2\ UO_3$ and added this to the leadless glaze. The result was the same crystalline glaze, even the red color appeared, and

*Conf. Riddle, Trans. A. C. S., Col. VIII, page 210 and Minton, Trans. A. C. S., Vol. IX, page 777.

this seems to be sufficient proof, that the cause is not a segregation of lead or any of its compounds, but a certain crystallizing substance, in the composition of which bismuth and uranium combined are the main parts. That the combination of both is necessary was proven by the fact that neither of the two elements alone would produce the same effect.

According to my idea bismuth oxide in consequence of its strongly basic nature, endeavors to form a crystalizing compound with uranic acid, for which process a neutral or basic glaze will furnish the most favorable condition. The glazes which showed the best result, were constructed according to the following two formulas:

$$\text{A.}\quad \left.\begin{matrix}0.25\ PbO\\ 0.20\ Bi_2O_3\\ 0.10\ CaO\\ 0.05\ MgO\end{matrix}\right\} = 0.60\ R_2O \left\{\begin{matrix}0.05\ Al_2O_3\\ \\ \end{matrix}\right. \left.\begin{matrix}0.75\ SiO_2\\ 0.25\ B_2O_3\end{matrix}\right.$$

$$\text{B.}\quad \left.\begin{matrix}0.20\ Bi_2O_3\\ 0.16\ K_2O\\ 0.08\ MgO\\ 0.16\ CaO\end{matrix}\right\} = 0.60\ R_2O \left\{\begin{matrix}0.05\ Al_2O_3\\ \\ \end{matrix}\right. \left.\begin{matrix}0.75\ SiO_2\\ 0.25\ B_2O_3\end{matrix}\right.$$

Unfortunately other duties prevented me from further studies on the subject, and I must confine myself to have been the first to call attention to this peculiar action of bismuth and uranium, and to have obtained crystals at as low a temperature as Seger Cone 010-09. The trials were successful on Seger porcelain as well as on a hard fired white granite (*Steingut*).

Another new crystallizer, which I discovered during the same period, 1901-1902, is tungstic acid WO_3, which, however, yielded the desired result only at the much higher temperature of Seger cone 8-10. Experimenting with lead glazes, which were to be non-poisonous according to the sense of the German law, about which I reported in the Sprechsaal, I also made trials with Wolfram trioxide and observed in pouring the red-hot melted fritt on a cold iron-plate, that the originally clear glass started to show a scum, which increased until the whole glaze became perfectly opaque. Further experiments demonstrated that opacity began sooner and increased quicker the higher the

percentage of Wolframic acid. As a rule 10% was sufficient to cause spontaneous and perfect opacity during the process of cooling. Melting such glasses on vases of Seger porcelain, those which contained much alumina and were rather clammy, would not form crystals even at high temperatures (cone 8-10), while those with less alumina and more or less liquid showed decided inclination to become crystalline. I experimented with glazes of the following formulas:

a. $RO—2\ SiO_2—0.1\ WO_3$
b. $RO—2\ SiO_2 \cdot 0.25\ B_2O_3 \cdot 0.1\ WO_3$
c. $RO—2\ SiO_2 \cdot 0.50\ B_2O_3 \cdot 0.1\ WO_3$
d. $RO—2\ SiO_2 \cdot 0.75\ B_2O_3 \cdot 0.1\ WO_3$
e. $RO—2\ SiO_2 \cdot 1.00\ B_2O_3 \cdot 0.1\ WO_3$
f. $RO—0.1\ Al_2O_3 \cdot 2\ SiO_2 \cdot 1.00\ B_2O_3 \cdot 0.1\ WO_3$

In these formulæ RO was composed as follows:

$$RO = \begin{cases} 0.50\ PbO \\ 0.30\ CaO \\ 0.10\ K_2O \\ 0.10\ Na_2O \end{cases}$$

All of these glazes showed more or less of a scum, and accordingly their surface was rougher or smoother. All of them were inclined to form crystals, the most perfect ones being obtained with glaze f, which sometimes showed very peculiar formations. Raising in this glaze the amount of silicic acid to 3 SiO_2 corresponding to the formula g) $RO.\ 0.1\ Al_2I_3 \cdot 3\ SiO_2 \cdot 1\ B_2O_3 \cdot 0.1\ WO_3$ did not improve the effect. Better results were reached by mixing glazes a, f, and g, which developed very interesting fernlike and star-shaped formations. The crystalline segregations are entirely different from the well known zinc and titanium crystals, and show partly peculiar iridescent reflexes, which makes these crystals to appear very distinctly although they are not colored by any oxide. A few additional experiments demonstrated, however, that it is also possible to have the crystals colored with splendid effects. I am sorry to state that in this instance also I was unable to follow up the matter, and I will be very much pleased if this first communication will instigate some one else to further investigation.

THE NEW POTTERY AND ART TERRA COTTA PLANT OF THE VAN BRIGGLE POTTERY COMPANY AT COLORADO SPRINGS, COLO.

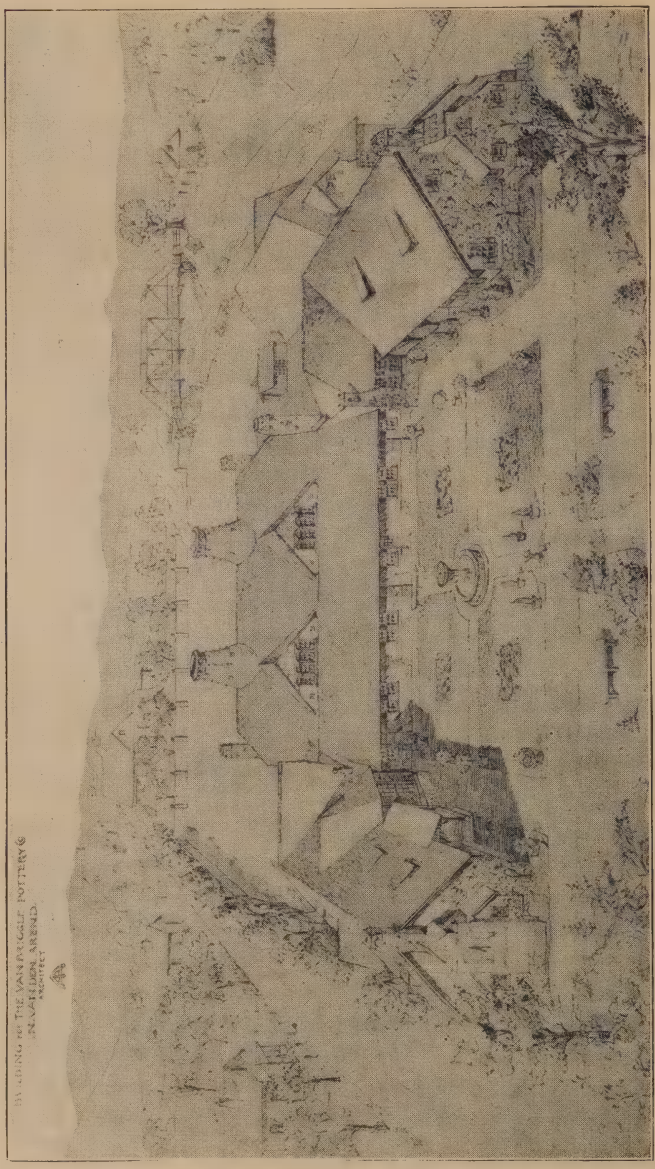
BY

FRANK H. RIDDLE, Colorado Springs, Colo.

Experience has shown that the location of an art pottery does not depend as absolutely on the proximity of raw materials or market as the majority of other clay working industries. However, the proximity of these raw materials aids very greatly, especially when terra cotta is included in the output of a plant.

The location of the Van Briggle Pottery at Colorado Springs has a great many favorable features. The city and its beautiful surroundings attract thousands of tourists every year. These tourists are looking for the unusual and the beautiful, and devote their time to nothing else but the search for these. The yalso wish souvenirs as remembrances of the places they have visited, and wish them to be something entirely characteristic of the locality. They have long ago become tired of buying Indian relics which are manufactured by the thousands in the East. They start out with the expectation of spending money, and consequently are willing to pay a reasonable price for characteristic products. If they visit the plant and see the products in the various stages of manufacture these products are still more interesting and more to be desired.

A collection of dirty, smoky, tumbled-down buildings, or even the usual factory building down on a railroad or on the outskirts of a city is neither unusual or beautiful, and is the last place to attract people. To overcome this defect and to make a place easily accessible this plant was located in a beautiful park very close to the business portion of town, and also where it could be seen from one of the main drives taken by the sight-seeing public. This particular


BUILDING for THE VAN BRIGGLE POTTERY &
MAURICE ARENS
ARCHITECT

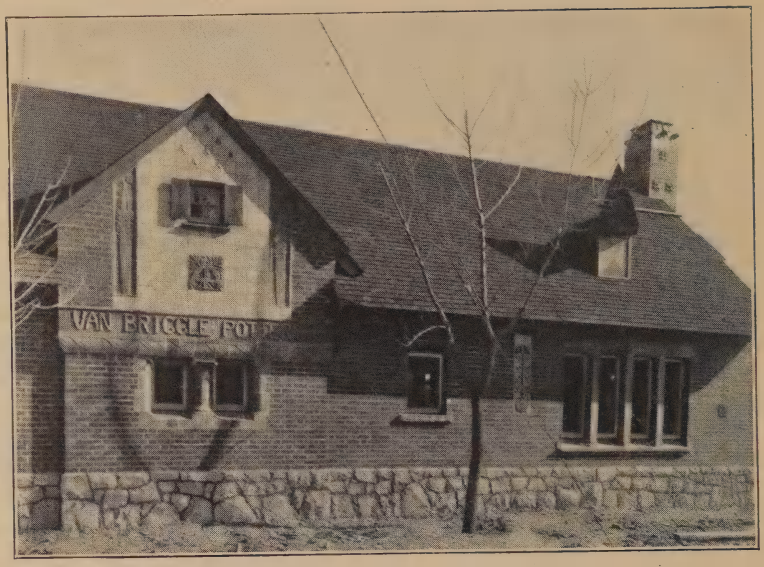
location also puts the building about three blocks from the best residence portion of the city, and makes it convenient for the town people as well as the tourists. It is also about 200 feet from the main line of two railroads, so that a spur can be put in if occasion demands.

The building itself was designed with a view of having not only a properly built factory but also having the exterior, salesroom, etc., very beautiful and attractive, and decorated entirely with the products of the plant. This company operated a small plant in another part of the city for several years before moving into the new one, and made all the decorative work for the new plant there. The style of architecture enables the builders and architects of the locality to see what beautiful effects can be produced by the use of clay wares, and at the same time shows just what can be produced at this particular plant.

The accompanying cuts show the general method of design but do not bring out the colors, which add a great deal to the general effect. The building is of brick laid in Flemish bond and a great many black headers used. The roof is of a dark green. To break the monotony a great many highly colored matt glaze tiles are used, ranging from turquoise to green, yellow and plum colors; also glazed terra cotta, as well as the natural colors. Again, a combination of iridescent and matt glazes is used. To some people, especially those living in gray, foggy localities, these colors would seem peculiar, but Colorado is a bright sunshiny place, and all the color schemes are arranged with a view of the surroundings.

It will be seen from previous statements that the local trade is no mean factor in the business. Again, art pottery is light, and can be shipped to the various markets as well from this section as any other.

The plant was designed with a view of making as wide a range of products as possible, and these in rather small quantities. This requires a very complete set of machinery of small capacity. The out-put of the plant is matt glaze art pottery, small pieces of glazed terra cotta for mantels,


VAN BRIGGLE

chimney tops, interior decorations, and repress tile for the same work, dry-press tile for hearths, and also flower pots and garden decorations.

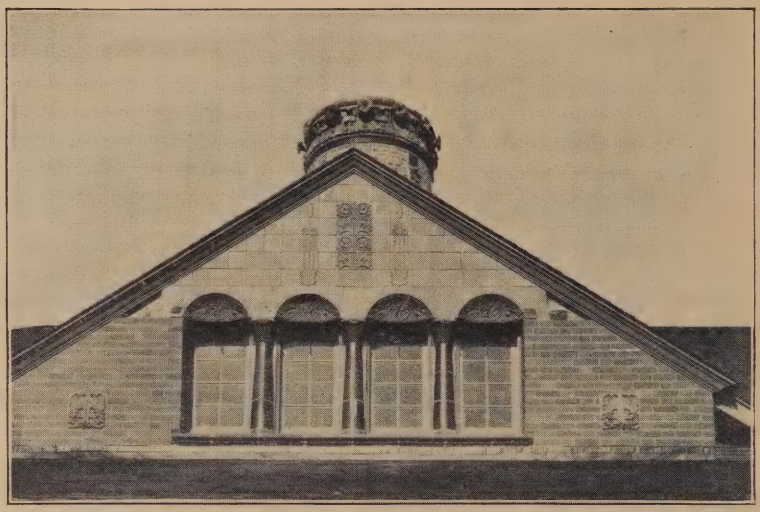
The raw materials for the above products are close at hand and in large quantities. For a description of Colorado Clays see Transactions A. C. S., Geijsbeek, Page 98, Vol. VIII. Within five miles of the plant are deposits of clay ranging in color from dark red to cream buff, and in quality from a fair grade of fire clay to an unusually refractory red-burning clay, that is, a red-burning clay which matures at about cone 4-6, as compared with the usual red-burning clays maturing at cone 06-1. There is also a two-foot vein of real flint fire clay. The above range of clays covers all the kinds necessary at this plant. The light buff clay is used for pottery, buff tile, terra cotta, saggers, etc., and the red clay for flower pots, dry-press floor tile, dark red terra cotta and similar wares.

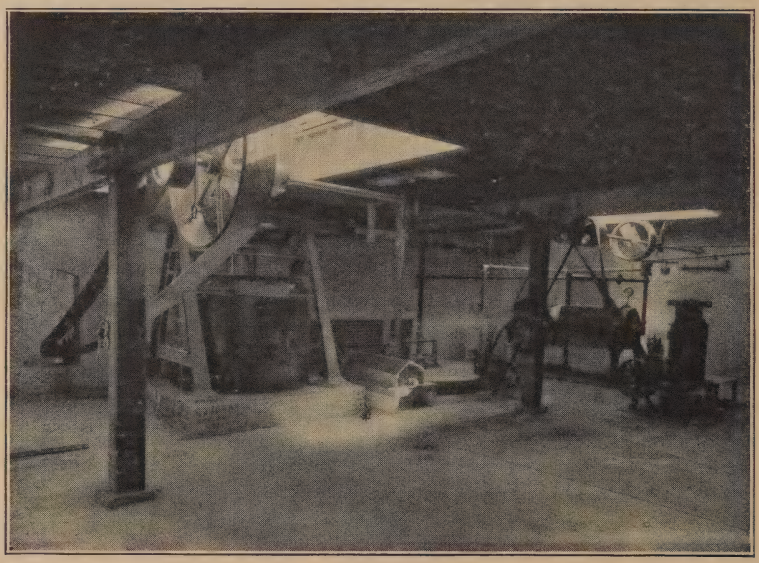
MECHANICAL EQUIPMENT

Electricity is used for power, and is distributed about the plant by five separate motors. The entire power required is 37½ H. P. This small amount of power is obtained from a local power plant at a rate much cheaper than it could be made.

The machinery for clay preparation consists of a complete clay-washing plant. This furnishes the casting, throwing and jigger clay, also the filtered clay for the dry-press tile. For this purpose the clay after leaving the filter press is dried, broken up, the desired amount of water added and then run through the dust mill, screened and stored. It might be stated here that the same natural clay, without the addition of any flint or spar, is used successfully for all the above-mentioned things, so that the clay required for each department is taken out when in the proper stage.

A combination dry and wet pan is used for the grinding of clay and grog and the tempering of sagger, wad,





repress tile, and terra cotta clay. A potter's pug mill is also used for part of the above.

Most of the pottery is cast, some few large pieces pressed; and bowls, beer mugs, plates, ash trays, and similar shapes jiggered. The mechanical equipment for the manufacture consists of a power throwing-wheel, a kick-wheel, a pull-down and jigger, and a dry-press tile machine. The jigger is designed for all sized work and a small head will be used for small work, and larger for large work. A small lever pull-down is used for ash-trays, plates, etc.

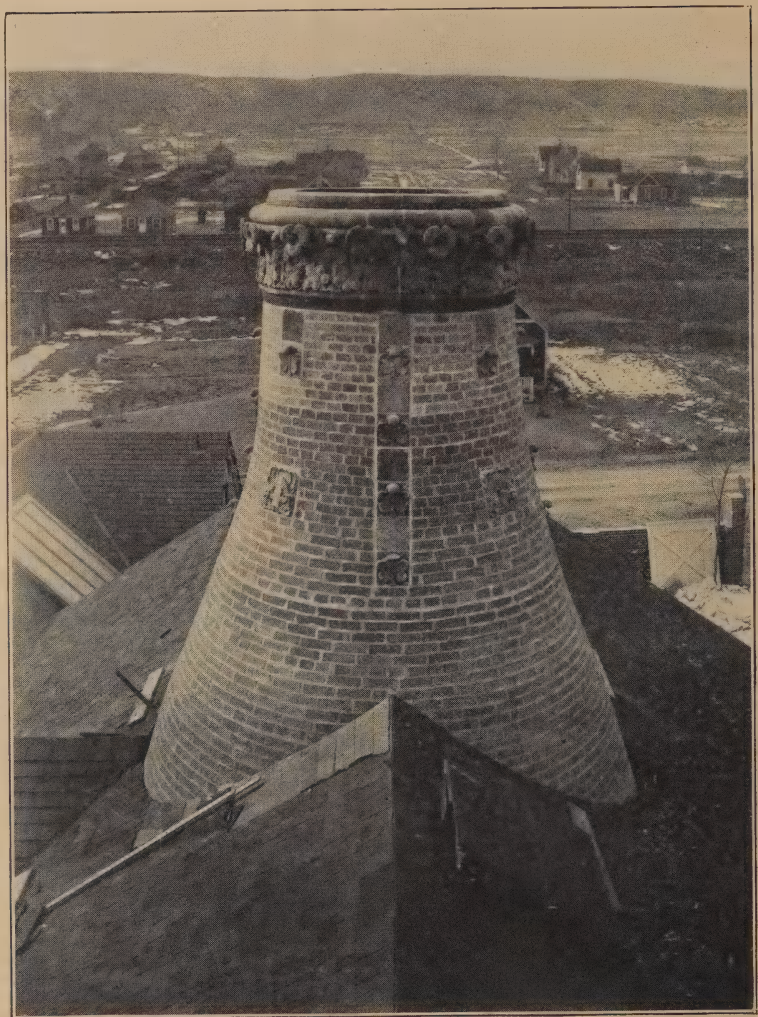
The drying is a very small problem, as the clays are rather open and the atmosphere is extremely dry. In summer all casting moulds are dried in open air.

KILNS.

The burning is done in regular potters' up-draft kilns. The terra cotta is small work and of high quality, so it can be saggered all right. The burning is perhaps the hardest problem the plant has to contend with. Horizontal grate bars are used because the fuel is not suitable for dead-bottom boxes, and again the firemen obtainable in this section of the country have never seen anything but boiler fire boxes.

The fuel used is a lignite for the beginning and up to red heat and a bituminous coal, known as Maitland, for the higher heats. The lignite is hauled directly from the mines only about two miles off, and the better coal is carried by rail from Canon City, a distance of about eighty miles.

A glance at the cut of the interior of the kiln house will show a rather peculiar construction at the fire boxes. The location of the plant is such that an excessive amount of smoke would be very objectionable, consequently the boxes were so constructed that most of the air goes in over the fire boxes. This was done not only with the hope of making more nearly perfect combustion, and consequently little smoke, but also to drive the flames to the well-hole of the kiln and thus keep the bottom hotter. At the old plant the kilns were the same with the exception of the air



holes over the boxes, and the fact that the fuel was fed in through a hole in the top of the hub instead of through a fire door at the side. The old way required two men, one to pull covers and the other to feed the fuel. It also allowed fresh fuel to go on to the hottest part of the fire box and produce enormous volumes of smoke, and also send the heat directly up the bags. The present way one man fires and puts the fresh fuel in the cool part of the box and gradually cokes it before shoving it to the hotter parts. Actual operation of both these kilns by the same fireman, and loading in the same manner, has shown that much better results are obtained with the over-draft box, not only in producing less smoke but also in obtaining more uniform burns. However, the latter are much more sensitive to slight changes and require more constant attention.

GLAZE DEPARTMENT.

Perhaps the only unusual part of the glaze department is the method of the recovery of glazes. A good part of the art ware is not dipped but sprayed with an atomizer. The spraying is done in small sheet iron booths similar to those in common use. The surplus glaze is sucked out by a fan, but instead of being blown away it is sent through a separator and recovered. Of course this cannot be done when glazes of different chemical formula are used, but it is satisfactory when the same glaze with different colors is used. In this case a large batch of the recovered glaze is screened and tested for color and corrected. Of course only dark colors can be produced, but they are usually very fair greens. In this way all the waste glaze from the pottery is used on tile.

The glaze-grinding room is equipped with ball mills entirely, and is of sufficient capacity to grind all the raw glaze materials necessary. Most of these are obtainable from local out-crops. The plant has a complete chemical laboratory in connection, so that these local materials can be tested and used satisfactorily.

Where the methods and equipment have not been mentioned they are very similar to the common methods which would be used in a plant of similar character.

The building is divided into three main departments, the manufacturing, art, and executive department. The executive department consists of office, salesroom, gloss ware house and packing room. These departments, although separated, are in the proper position in relation to one another. The manufacturing department is equipped with cement floors throughout as well as electric light and steam heat.

One objection raised by some people at being out of a pottery center is the trouble to get skilled labor. This plant in seven years' experience has found that with one person having a general knowledge of manufacture in all the branches and a good practical potter as thrower, turner, and mould maker, common laborers can be taught the rest with fair success. At present the force has a jiggerman, mould maker, kilnman, sagger maker, trimmers, and in fact all the required helpers. With the exception of the two mentioned above not one of these employees has ever been in a pottery before. Of course the teaching requires patience and some loss, but most of the employees worked around when the pottery was smaller and have grown with the plant. Again, in a small place the men will be thrown from one job to another and so become skilled in several branches. Experience has shown, however, that it is wise to always have at least two who can do the same work. The cost of labor is no more than in pottery centers, and in such a small force as is required in this plant, organized labor has not much chance to assert itself.

POTTERY PLASTER.

BY

HARRISON EVERETT ASHLEY, Newell, W. Va.

This paper will be divided, in a measure, into a consideration of the occurrence of gypsum and the manufacture of plaster, the chemistry of plaster, and various tests made by the writer on pottery plaster. Although other sources have been consulted, the first part of the paper has been largely extracted from a work by G. P. Grimsley on "The Gypsum of Michigan and the Plaster Industry," published under the direction of the Board of Geological Survey of the State of Michigan.

Gypsum is a mineral whose chemical formula when pure is $CaSO_4 (H_2O)_2$, and whose composition is Lime (CaO) 32.5 per cent., Sulphuric anhydride (SO_3) 46.6 per cent., and Water (H_2O) 20.9 per cent.

It is one of the softest minerals, occurring in soft colorless, white or slightly tinted masses, which may be granular or compact, or may be translucent and silky, fibrous or transparent, and cleavable into plates and strips. The latter forms of occurrence are evidence of a crystalline nature, and well developed crystals are common.

At 18° Centigrade 1 part gypsum dissolves in 386 parts of water, at 24°C. in 378 parts.

Gypsum occurs in large beds with limestones, marls, and clays, and in volcanic regions with sulphur. It is found in many parts of the United States and other countries. The Michigan deposits are the largest producing in this country, but Ohio, New York, Virginia, Iowa, and some other states also produce considerable quantities.

The products are land plaster, retarded wall plaster, plaster of Paris, pottery plaster and dental plaster.

The manufacture of the last four plasters of the list above depends on the following chemical basis: When

gypsum is heated, it begins to give off water at 80°C. At 125° to 128° this action is carried on most thoroughly until three quarters of the total water has been given up. The formula thus becomes $(CaSO_4)_2\ H_2O$, and the product is plaster of Paris. From 130° to 150° practically no water is given off. Between 163° and 194° the remaining portion of water is given off, and the formula becomes $CaSO_4$. This action is fully completed at 200°. Plaster Paris, on being mixed with water recombines with it, forming a substance of the same chemical composition as the original gypsum rock. The fully dehydrated gypsum also recombines with water readily unless heated beyond 221°C., after which it will recombine and set only slowly. If heated beyond 343°, it is "dead burned," and will not set on addition of water.

These relations may be expressed as follows:

$$\left.\begin{matrix}CaSO_4\,(H_2O)_2\\ CaSO_4\,(H_2O)_2\end{matrix}\right\} \xrightarrow[80°\text{-}125°\text{-}128°]{-3\ H_2O} CaSO_4(H_2O) \xrightarrow[130°\text{-}150°]{-H_2O} \xrightarrow[163°\text{-}194°]{} 2\ CaSO_4 \xrightarrow{200°}$$

The typical Michigan process of manufacture (originally introduced from New York) is as follows:

The quarried rock is reduced by a jaw crusher to the size of a man's hand, by a cracker (mill with cones like a coffee mill) to the size of small gravel, and by ordinary buhr mills or emery stone mills to a coarse flour. This is elevated to bins and fed to calcining kettles. (Fig. I.)

(Fig. I is taken from page 120 of Grimsley's "Gypsum of Michigan.")

These consist of a hollow cylinder of ⅜" boiler steel, of equal width and depth, about 8 ft. or, more commonly, 10 ft. This is set on an iron ring. On the ring is also placed a ⅝" cast iron bottom, convex upward. Through the kettle pass two or four horizontal flues. A stirrer close to the bottom makes about 15 revolutions per minute, and uses 10 to 25 horse power. A 10 foot kettle calcines 3¼ tons gypsum per hour. "In an hour after the gypsum kettles are filled the temperature reaches 110°C., and the mass is seen to be boiling vigorously, as the water is driven

FIGURE 1. TRANS. AM. CER. SOC VOL X
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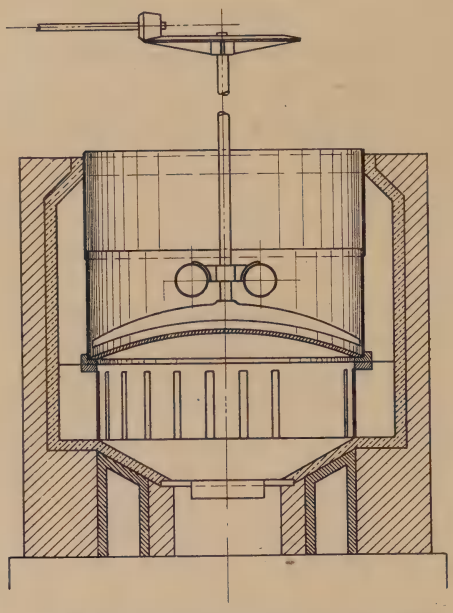

EHRSAM CALCINING KETTLE.

off and out through the vapor stacks above. When the temperature increases to 132°C. the gypsum settles down solid, leaving 16 inches or more of vacant space at the top, and the steam almost ceases to rise. At 138° to 143°C. the mass comes up again, often throwing a part of the material over the top of the kettle. When the temperature of 177° to 188° is reached, the plaster is readily withdrawn through a gate near the bottom, controlled by a lever above, into a firebrick bin on the ground, and the kettle is then refilled."

In some mills a few years ago, and occasionally at the present time, the plaster was drawn after the first setting. This method would enable the manufacturer to make plaster in a shorter period of time and so increase the capacity and lower the cost of fuel and labor. "Such plasters have not been received with satisfaction by the trade. They are of lower strength and are often rejected by plasterers."

"In a specimen of the Michigan plaster obtained from one of the mills, the water percentage after the first settling was 5.70 per cent. This analysis would not condemn the plaster in the first sample. It is similar to the amount in the Blue Rapids plaster of Kansas, which is a standard grade of plaster."

"The formula of the calcined plaster $(CaSO_4)_2\ H_2O$ calls for 6.2 per cent. of water and 93.8 per cent. of calcium sulphate.

The calcined plaster is elevated to sloping shaking screens. The tailings are ground. The mesh of sieves is in

Western United States.....30-35 per linear inch
Michigan and Ohio.....35-45 per linear inch
New York .....40-45 per linear inch

One of the manufacturers of pottery plaster uses a disintegrator and air separator instead of a screen.

To the wall plasters a retarder is now added in a mixing machine. The retarder is generally of a glue-like nature. Some of the ingredients used are glue, hair, saw dust, blood, tankage, etc. Plaster Paris would "set in a few minutes," but four to six pounds retarder per ton will delay set three to four hours. Unless specially ordered, wall plasters are mixed to delay set about two hours. A retarded plaster is weaker than an untreated plaster.

There are two theories as to the action of retarders. One is that by holding the water, as dried organic tissues have a strong affinity for water, the retarder gives the water up but slowly to the plaster, and the crystallization is delayed. The other is that glues increase the viscosity and hence retard circulation. The growing crystal soon exhausts its immediate neighborhood and new material is only slowly fed in. This seems the more probable. The discussion of setting should properly have preceded mention of retarders.

Theoretically when 18 per cent. of water is mixed with plaster Paris, it recombines with it, and forms a substance of the same chemical composition as the original gypsum

rock. Grimsley says, "To obtain all the strength of the plaster it is stiff gauged by adding very little water."

Thorpe says (Industrial Chemistry, p. 163) that 30-35 per cent. is practically used. In my test work, I find it necessary to use 75 per cent. to get a thorough mixture by stirring.

Weelans (Trans. Amer. Cer. Soc. IX, p. 193) states that 85-95 per cent. water gives the best results for some classes of mould making for sanitary pottery.

Under the microscope, it is found that the entire mass of set plaster consists of interlaced crystals. "According to Le Chatelier, the plaster of Paris compound $(CaSO_4)_2$ H_2O dissolves in part of the added water, which diminishes the solubility, and the solution becomes therefore supersaturated and $(CaSO_4)_2$ H_2O, or gypsum, crystallizes out. In other words, the plaster of Paris dissolves, and becomes hydrated, then crystallizes out as gypsum, and every particle of the plaster goes through these steps.

According to my own theory, which is based on the work of Le Chatelier, and others, and on the testing methods to be described further on, the plaster of Paris is first hydrated, then dissolves in water, then crystallizes out as gypsum. The hydration is acompanied by a rise in temperature. The hydrated plaster coats masses of unhydrated plaster that the water fails to penetrate to at first. This causes a halt in the process of hydration. The excess of free water at once begins to dissolve the hydrated plaster. This reaction may be sufficiently energetic to lower the temperature for a period that may extend to 15 or 20 minutes with pottery plaster. When the water becomes saturated, gypsum $(CaSO_4)$ 2 H_2O starts to crystallize out. As soon as crystallization starts, the set begins, and proceeds more and more rapidly for a time until nearly complete. The temperature rises rapidly. This is because the growing crystals furnish a place to deposit the dissolved plaster; the water therefore dissolves the more soluble noncrystalline hydrated plaster more rapidly, uncovers the still unhydrated plaster, and hydrates it, thus developing

heat in considerable quantity. The more finely ground a plaster is, the more extensive is the initial hydration, the more rapidly is the water saturated with hydrated plaster, and the sooner does the set, or crystallization, commence. The prime mover of these actions is the energy of hydration, supplemented by the solvent action of water, and the difference in solubility of uncrystallized and crystallized ($CaSO_4$) 2 H_2O.

Plaster of Paris may be hardened by mixing alum, borax, or tartaric acid with it, or by adding some alcohol to the water with which the plaster is mixed. However these substances retard the setting, and most of them decrease the porosity, which must be preserved for pottery purposes.

Tests.

Sieve. The first test I make is to sieve 50 or 100 grams through an 80 mesh sieve. (31.5 meshes per linear centimeter.) The residue obtained on the sieve is very troublesome to mouldmakers; as instead of staying suspended in the water used for blending, it sinks to the bottom of the can. If in the plaster poured for moulds that have to be scraped, the hard lumps cause long unsightly scratches on the scraped surface. Chemically this coarse matter is as much plaster Paris as the fine stuff, but mechanically it is very objectionable.

Tensile. I do not use the popular tensile strength test. A few observations from Grimsley will be of interest. A lot of plaster exposed to atmospheric conditions for a year in an unheated room decreased in strength from 595 to 536 pounds on 1 month briquettes. A number of tests put out doors as soon as set and kept out for a week with a temperature below 0°C. showed an average of 500 pounds. Samples of underburned plaster (high percentage of water by analysis) broke under 100 pounds, tests of overburned plaster broke at 150 pounds, tests of properly burnt plaster of the same brand broke at 426 pounds. Underburning appears to be a greater evil than overburning, as far as

strength is concerned; but for pottery purposes, underburned is better than overburned. Standing in water decreased the strength.

Heating. In a German work I found it mentioned that the strength of plaster Paris may be measured by the heat evolved on mixing it with water. Shortly after this, the following information came from a prominent manufacturer: "We take a small quantity of plaster, say about three-quarters of a pound, mixing same with enough clean water to make a stiff paste, on a slab of glass or marble. When it hardens sufficiently to support itself we insert a thermometer in the paste. When it begins to set quite hard the cake will begin to show heat and the heat will increase until it is fully set. Then the mercury will begin to drop. That usually takes from 35 to 45 minutes and shows that the plaster is set, but the plaster is hard enough at from 28 to 30 minutes so that you can make no impression in it, and that time we call the time of set, but actually by the thermometer there is a few minutes longer of action going on, though the plaster does not seem to get any harder, or enough harder to tell it by our methods. The thermometer usually shows in winter from 75 to 80 degrees. Then the action in the plaster stops. In the summer it runs up to 90 and 100 degrees, depending how warm the weather is."

Starting with the above information, I developed the following *heating test*: 75 grams water is put in a cup and its temperature determined. 100 grams plaster is added, and rapidly stirred to a uniform consistency. A thermometer is inserted and readings taken of time and temperature.

Figure 2 shows results obtained by this method on

Dental plaster with 0.74% residue on 80 mesh.

An American Pottery plaster with 1.10% residue on 80 mesh.

An English Pottery plaster with 0.54% residue on 80 mesh.

Common Plaster Paris with 12.90% residue on 80 mesh.

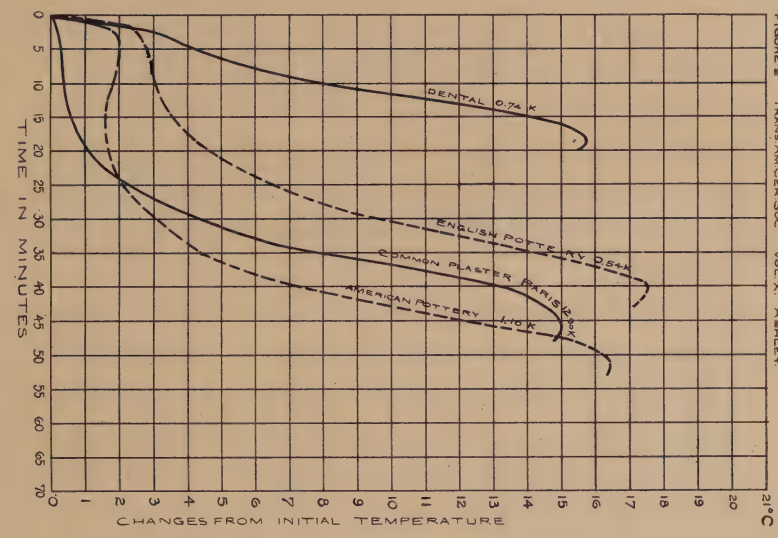

FIGURE 2. TRANS AM CER SOC. VOL X. ASHLEY.

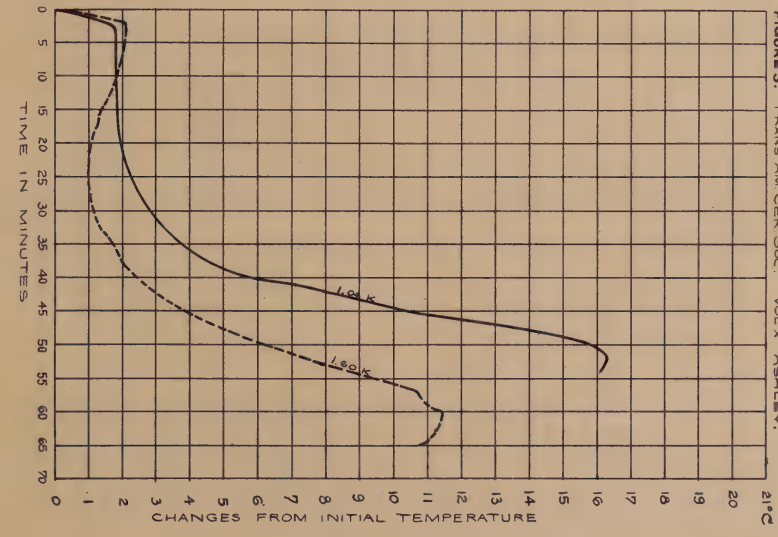

FIGURE 3. TRANS AM CER SOC. VOL X ASHLEY.

While the figures above show how coarse, they do not show how fine. The latter information is given in the lower left hand corner of the diagram by the rapidity of the initial rise in temperature (heat evolution because of hydration of plaster).

According to my theory of set, this rise should be the larger and more rapid the finer the plaster, i. e., the greater the surface of the plaster exposed for a given weight of material to the action of water.

Following the initial rise comes a retardation, or even a fall, in the case of the American pottery plaster sample. This is due to solution of the hydrated plaster in water, a phenomenon accompanied by a cooling effect, an absorption of heat. In the case of the dental plaster the solution is effected very quickly, so that the process of hydration is but little retarded. With the pottery plaster, solution is much slower, and only at the end of 20 or 25 minutes is a second very decided rise in temperature noted. At this time, the mixture in the cup ceases to be fluid, and assumes a solid look, energetic crystallization has set in, though still quite soft to the touch. The common plaster Paris is much coarser, solution and crystallization start so slowly and gradually that the entire curve is very smooth.

All these samples have been calcined to about the same extent, as is shown by their heating about the same amount. I am not able to explain why the finer American pottery plaster is slower than the coarse plaster Paris in reaching its temperature maximum. Possibly it is "retarded" a little; but this is a mere guess.

The sample of English pottery plaster was received after the foregoing was written. It is intermediate in fineness between the American pottery plaster and dental plaster.

These heating curves cannot always be confidently relied on for a full description of the character of a sample of plaster, but are a very convenient basis for comparisons. Fig. 3 shows curves obtained from two barrels of pottery plaster in the same car-load and of the same date, and

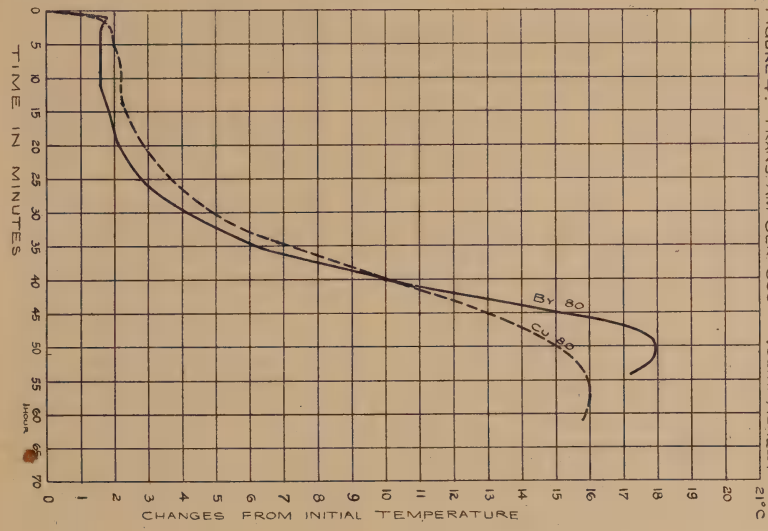

FIGURE 4. TRANS. AM. CER. SOC. VOL. X. ASHLEY

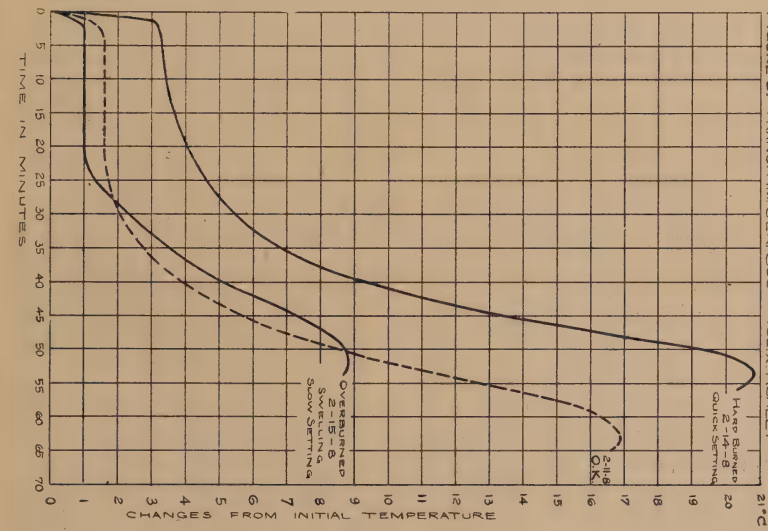

FIGURE 5. TRANS. AM. CER. SOC. VOL. X. ASHLEY

illustrates the variability of plaster as now manufactured. The coarser plaster was the slower in starting to crystallize and the slower in reaching final set; it was also not so well burned as the other barrel.

Figure 4 shows the difference between the coarse matter retained on an 80 mesh sieve and the fine matter passing the same. The fine matter is slower starting to crystallize, but reaches final set the earlier. It is better burned, or contains less inert matter, as is shown by the higher temperature attained.

Both the fine and coarse portions of this test were neutral to litmus. The temperatures used in calcining gypsum are so low that any carbonate of lime present would not be decomposed, and no free lime plays a part in the setting of pottery plaster.

Ageing. The phenomena of "ageing" moulds are probably in close relation to those of setting. We may make a few conjectures on the process as follows: Many chemical substances when formed by wet processes may readily be redissolved by proper solvents; but if allowed to stand or age a while become difficultly soluble or wholly insoluble. It is possible in these cases and very probable in the case of gypsum plasters, that this is a process of crystallization. It has been repeatedly observed that when large and small crystals are both present in the same solution, that the large crystals grow at the expense of the small ones. If this is so, we have a reason for the greater wearing power of aged moulds (estimated at 10% by Mr. Herford Hope). It might be said that the ageing process should be expected to continue in the clay shops; but it must be borne in mind that each piece of clay shaped on the mould leaves in it soluble salts, colloidal matters, etc., which tend to stop processes of crystallization.

Drip Test. Another test used by me is to put the formed piece under a water faucet that is dripping with a small unsteady stream, and allow it to stay there one hour. The result of this combination of mechanical and solvent wear is that the piece assumes the appearance of moulds that are ready to be discarded from the clay shop. Hard

lumps appear raised above the surface, and there are numerous air pits uncovered.

The uncovering of these air pits usually makes the irregularity of surface that necessitates discarding a set of moulds.

I have experimented some as to means of getting out the air more thoroughly than is common in ordinary blending.

First, I blended the plaster with boiling water. It partially accomplished the desired end; but, as might be expected, so accelerated the set as to make the method impracticable.

Second, I blended plaster and water in a ball mill. In one and three quarters minutes the rattling sound in the ball mill ceased. The grinding action of the mill had so accelerated the hydration that this method is impracticable. Third, I blended the plaster and water in a small blunger. After the plaster was all wetted, bubbles of air rose to the surface until I stopped the mill to pour the plaster. The air bubbles were reduced in number and especially in size, when tested by the drip test.

Vitrifying Action of Moulds. The effect of moulds on ware is of interest. Dippers have told me that one surface of certain lots of ware was softer than the other. On examination I found the hard side to be the side that was next the plaster mould in forming.

I made the following tests: Cast body trials were made on new and old moulds, in each case starting with a dry mould, which was dried as rapidly as a drying closet would work, and also starting with a wet mould which was allowed to stand out in the room over night before putting into the drying closet.

The results on fire shrinkage of the body were as follows:

	New Moulds.	Old Moulds.
Dry	7.40%	7.4%
Wet	7.35%	7.5%

The differences were less than the possible errors, so no light is thrown.

The results on percentage of water absorbed by the body were as follows:

	New Moulds.	Old Moulds.
Dry	7.2%	7.1%
Wet	6.8%	6.2%

The differences here are greater than the probable errors, and show that ware made on wet moulds is vitrified to a noticeable extent by the sulphate of lime dissolved from them.

Additional Note on the Expansion and Swelling of Plaster.

Grimsley* says: "I tried to determine the expansion in setting or the relation of the dry plaster to the set plaster, in volume. I could detect no expansion by direct measurement and by filling a thin glass bottle with mixed plaster and permitting it to set, in this case the bottle was not broken or cracked. I could not run in a colored liquid around the plaster, so apparently it did not shrink."

In my discussion of the drip test, I believe it is made plain that it is well nigh impossible to blend plaster without including therein a multitude of air bubbles. Consequently, if expansion of the plaster occurred in Mr. Grimsley's experiment, these bubbles of air were compressed a corresponding amount and the bottle was not cracked or broken. It did not shrink.

The experience of mouldmakers in making in plaster cases moulds to fit exactly the iron ring of a jigger is that unless the cases are reinforced by a hoop of iron, the plaster will swell the cases so that the moulds made in them are too large to fit the jigger rings.

The writer has recently had some experience with a lot of plaster, part of which swelled after taking from the

*The Gypsum of Michigan, p. 3.

cases. This plaster was complained of by mouldmakers as "soft." It did not heat up as much as usual for them, and was said to be slow in setting. It was difficult to get out of the cases.

This brand of plaster ordinarily tested by the heating test showed a rise of 17°C., rarely 18°, in about 50 minutes. Occasional barrels had fallen as low as 12° with no complaint other than of soft moulds. A barrel marked 2-13-8 tested 11.6°, confirming the complaint of softness.

But when the first lot of moulds were taken to the jiggerman, it was found that they had swelled up after taking out of the cases so as to stand as much as a quarter of an inch out of the jigger ring; and it was necessary to take them back to the mould shop for turning down to size.

A sample of each date was then tested as follows (Fig. 5):

Barrel marked.	Total rise.	Time in minutes.	
2-10-8	19.0°C.	53	
2-11-8	16.9°C.	63	
2-12-8	19.0°C.	61	
2-13-8	11.6°C.	56	Swelled
2-14-8	20.8°C.	53	
2-15-8	18.5°C.	62	
2-15-8	8.8°C.	53	Swelled

Most of these rises are uncommonly high, and tend to show that the makers had been burning the plaster higher than usual, and that the low result with the 2-13-8 and 2-15-8 barrels were more likely due to overburning than to underburning. The suggestion was made by Mr. Meakin.

This was confirmed as follows: A sample of each date was weighed, in a cup, put through a burn in the draw-through of a glost kiln, and reweighed. The percentage of loss was the measure of the water in the plaster.

Theoretical loss 6.2 per cent.

Barrel marked 2-10-8, 6.8 per cent.

Barrel marked 2-11-8, 7.0 per cent.

Barrel marked 2-12-8, 6.4 per cent.

Barrel marked 2-13-8, none on hand.

Barrel marked 2-14-8, 7.0 per cent.
Barrel marked 2-15-8, 6.4 per cent.
Another barrel marked 2-15-8, 4.6 per cent, overburned.

The mouldmakers had complained of 2-13-8 and 2-15-8 barrels. The others were in another shipment.

Referring back to the first of this paper, we may repeat that when plaster has been heated beyond 221°C. in making, it will recombine and set only slowly. And we may add that overburned plaster is the worst that can be given a mouldmaker.

DISCUSSION.

Mr. Mayer: Mr. President, this is a very valuable paper. Mr. Ashley has given us here a lot of information which I suspect is new to us all. His experience on this question I guess is a little deeper than that of some of us. It is always a difficult thing to attempt to criticise these papers when a lot of material is included which is new. I have not had much experience along that line. The information will be very valuable to us all, but I do not know that I have much in the way of criticism. I have learned much from the paper, I know that, and I think many others have also. Had Mr. Ashley been here there are some questions I might have asked, but I do not think I could discuss it at all.

The Chair: Since Mr. Ashley is absent it will be a difficult matter to start a discussion of his paper, there being no one to answer questions which might be asked.

NOTE ON TEXAS KAOLIN.

BY

ARTHUR MAYER, Beaver Falls, Pa.

Some time ago I hoped to be able to present at this meeting of the American Ceramic Society a paper on "Physical Properties of Glazes," but as the time of this meeting drew near it found my work on that subject far from complete.

A short time before this meeting I felt badly at not being able to do anything for the good of the work being done here, and resolved to give a few notes on the new Texas clay.

The object of these tests were to determine the value of this clay for use in either china or earthen ware, and also to investigate some of the peculiarities of this clay. The cost is not taken into consideration, as I have not heard a price quoted on it.

The location of the mine is about 75 miles west of San Antonio in Edwards County, Texas.

Physical Properties before Burning.

The sample received seemed, on examination, free from mineral impurities and quite free from moisture, being a snow white powder. The shipper assured me that this was the state in which it was taken from the mine without any treatment.

The division of the grains do not seem at all fine, as a sample was eleutriated and found to have a surface factor of only 9,036, which is quite small as compared to most English clays. For instance, J. M. clay has a surface factor of 16,570, V. C. S. F. 14,898, and Pool's No. 1 S. F. 16,798. Considerable grit could be felt in grinding some on the back of the hand. After blunging a sample for an hour it

gave 8.2% residue, showing that it needs some treatment before it is fit to put into a body.

The tensile strength of this clay is very great, being 89 lbs. to the square inch. Comparing this to china and ball clays a vast difference can be seen. The tensile strength on some well known china clays are: No. 1, 15.3 lbs. to the square inch, V. C. clay 29.8, Harris North Carolina, 28.1 lbs. to the square inch. Some ball clays have tensile strength as follows: 25.6 to square inch for Tenn. Ball No. 7, 35.3 for Whiteways, 39.5 lbs. for Edgar's Florida clay.

You can see that the tensile strength in more than any two of these other well known clays combined.

The plasticity is very great, and it takes 51% of water to make it into a workable state; if this water content is a true key to plasticity you can judge how great is the plasticity. When trying to mould this clay great difficulty was experienced an account of it being so sticky, much more than an ordinary ball clay.

The contraction from the mould to a white hard piece of ware is 10%. This is large, as most china clays shrink from 3½ to 4%.

Properties after Burning.

The trials were burnt to cone 10 bending, or 1320°C., and at this temperature there was practically no absorption, although ink would spot it so it could not be washed off.

The contraction due to fire was 12%, or a total shrinkage of 22%. This is exceedingly large for a china clay, as they usually average from 11 to 16% and ball clay from 16 to 19% for total shrinkage.

The hardness of the burnt ware is greater than that of tool steel, as when it is scratched with it it leaves a grey line of steel on its surface.

The color is one of the best points about the clay, and I have not been able to find any clay which will begin to compare with it for whiteness.

Chemical Properties.

With the exception of the fact that it is rather low in iron, it much more resembles a ball clay than a china clay. The beautiful white color must be due to two reasons, 1st, the low content of iron, 2nd, the bleaching out of the color by the high lime content. This high content of lime is also probably the cause of the great shrinkage by fire.

The following is an analysis of the Texas clay and a well known English clay, with which it can be compared:

	Texas.	Whiteway's Eng. Ball.
SiO_2	43.75	44.92
Al_2O_3	37.62	38.68
Fe_2O_3	.36	.92
$CaCO_3$	1.40	.74
$MgCO_3$	.....	.....
Loss on ignition	15.84	10.62
Alkalies	.96	3.68
	99.93	99.56

It is far ahead of all English or American clays now on the market, in color.

A trial body was mixed up as follows:

Spar	700
Calc. Carb.	88
Texas Clay	1560
Ball Clay	240
Flint	1412
	4000

This body was fired to cone 8, down, and would be a better body if it had a little more spar and fire. This piece of ware is translucent and well vitrified, and still is better in color than any earthenware made in this country. In the green state it had 142.3 lbs. tensile strength to the square inch, thus insuring small loss in placing the ware, etc.

In summing up all that has been said regarding this clay I have seen no china clay which will compare with it in color, vitrification, strength or plasticity, and can see no reason why it should not develop into the foremost of all American clays.

DISCUSSION.

Mr. Arthur Mayer: I might also state another peculiarity of this clay that I have not mentioned in the paper. When in the green state or in slip it has almost a waxy translucent appearance, and I am at a loss to account for this very peculiar phenomenon.

Dr. Zimmer: If the paper refers to a Texas clay, which is similar to those about which I read a paper before the Society at the meeting held at Old Point Comfort, Transactions, Volume 111, page 25. About nine years ago I received those samples of Texas Clays, and in the investigation of them I found they contained hydrated silicic acid. Since then, of course, the mines have been opened and no doubt the product is more uniform; but at that time the samples showed quite a variety. Besides the mines were too far from a railroad station to be of great commercial value. I have learned since, however, that the conditions have changed, and of late a company has been organized with the object to develop those clay mines in Texas. I was shown some very thin, and at the same time perfectly straight, purely white pieces of ware made of a body containing a high percentage of Texas Clay, coming from about the same place from which I previously received my samples. Furthermore, I was told that at least one factory has made satisfactory trials on a large scale; and this is the reason why I believe two additional analyses of samples, obtained shortly before leaving Germany, which were made at the laboratory of the Sprechsaal, at Coburg, will not be without interest. While they do not agree with that given by Mr. Mayer, they may be interesting as showing the variety of those clays and the possibilities of them.

SAMPLE IV, Very Hard.

Moisture and loss by ignition	20.90%
SiO_2	46.70%
Al_2O_3	28.34%
Fe_2O_3	0.86%
CaO	0.12%
MgO	1.65%
K_2O	1.64%
	100.21%

Of the combined moisture and loss by ignition 8.90%, H_2O was expelled by drying over concentrated sulphuric acid.

SAMPLE V, A Trifle Softer than IV.

Moisture and loss by ignition	19.78%
SiO_2	47.10%
Al_2O_3	29.68%
Fe_2O_3	0.72%
CaO	1.04%
MgO	1.16%
K_2O	0.97%
	100.45%

7.80% H_2O was extracted by drying over concentrated sulphuric acid.

In regard to the physical qualities, I can confirm what Mr. Mayer says; and I believe a good many of the phenomena for which he could not give an explanation would be explained by the fact that such clays contain amorphous silicic acid. We can obtain somewhat similar effects by adding water glass to kaolin.

Mr. Mayer: I would like to ask a question and see if any one can answer it, regarding the difference in tensile strength of this clay when made up into a body and when used alone.

Mr. Hottinger: I would say that I had a sample of probably this identical clay. I got mine through an agent in Chicago. I found the great difficulty in it was in the drying. You cannot dry it without getting a lot of cracks. While apparently the surface will be perfect, the interior will be full of fine hair-line cracks, and you don't see it until you break the burnt ware. I think this will account for the difference in tensile strength. If it is in a mixture with non-plastic ingredient it has a chance to dry and has remarkable strength.

Mr. Mayer: Only in the pure clay did I have any trouble with cracking. The disks passed around are all badly cracked you will notice, but when made into a body there seemed to be no cracking at all, and it worked very nicely indeed.

Mr. Fox: I never ran across a clay that worked exactly as this one. The nearest I came to it was a clay from down near Jerseyville, Ill. The clay was quite different in one respect from this. It has a very high tensile strength. The tensile strength, as I remember it, ran something over five hundred pounds to the square inch, varying from 500 to 560. The clay itself seemed, however, rather short. The content of non-plastic material was rather high. The clay would dry quite quickly and safely, and so from all its physical properties it ought to have shown a low instead of a high tensile strength. At the time the tests were made, I came to about the same conclusion as Dr. Zimmer arrived at in this case; that is, that there must have been present some amorphous silicic acid. This clay, as already mentioned, when dry gave a high tensile strength. I can see how mixing feldspar and flint with the clay under discussion might produce the same effect; and I presume Mr. Hottinger is right when he says the trouble with the clay in the raw condition is the difficulty of drying, probably due to the fine cracks mentioned. The introduction of non-plastic material simply opened it up and gave it opportunity for drying without cracking.

THE USE OF CORNWALL STONE VERSUS FELDSPAR AS A FLUX FOR PORCELAIN.

A NOTE

BY

A. S. Watts, Victor, N. Y.

So much has been said and written regarding the value of Cornwall stone as a flux that I determined to make a few tests to ascertain what value it might really have as a porcelain ingredient.

I first obtained a quantity of Cornwall stone on which an analysis was obtainable. It proved very fine grained and clean and had a formula

$$\left.\begin{matrix}.676\ KNaO \\ .293\ CaO \\ .030\ MgO\end{matrix}\right\} 1.167\ Al_2O_3\ \ 8.93\ SiO_2$$

Combining weight—732.7

The objection heretofore offered was that the raw clay content varied, as did also the free flint, when a duplicate body was made with Cornwall stone and with feldspar and a comparison was attempted. To overcome this objection I determined to make up and fritt a mixture duplicate in composition to the Cornwall stone used. In producing this I used a feldspar having a formula:

$$\left.\begin{matrix}.772\ KO \\ .148\ NaO \\ .069\ CaO \\ .011\ MgO\end{matrix}\right\} 1.08\ Al_2O_3\ \ 6.44\ SiO_2$$

Combining weight—617

The substitute for Cornwall stone had the following per cent composition:

Feldspar noted above	58.37%
English China Clay	12.42
Rock Flint	26.67
Fluorspar	2.43
MgO (calcined)	.11
	100.00

The fluorspar was substituted for whiting in order that any additional fluxing value possessed by this form of calcium over the other forms, might be taken advantage of in this experiment. The substitute was mixed intimately in the dry state and placed in a sagger and fired at cone 10. The fritt produced was a very peculiar glassy slag of a light cream color and full of bubbles, which indicated that a violent boiling action had occurred. This slag was broken up and ground and passed through a 120 mesh screen. A body was chosen for this experiment having the following formula:

$$\left.\begin{matrix} .16\ K_2O \\ .08\ CaO \end{matrix}\right\} 1.0\ Al_2O_3\ \ 4.5\ SiO_2$$

This body is the same as is used in my other paper* and is the same as No. 3 in K, L, M and N Series. By this means we have already for comparison this body made with feldspar and whiting, with feldspar and pulverized marble, with feldspar and plaster of Paris, and with feldspar and fluorspar. We will now proceed to make it up with Cornwall stone and artificial Cornwall stone as follows:

"P" Body.

43.69%	Cornwall Stone, *Genuine*
.10	Whiting
34.00	English China Clay
8.00	English Ball Clay
14.17	Rock Flint
99.96	

*"The Action of the Different Forms of Calcium as a Flux in Porcelain Manufacture," this volume.

"Q" Body.

43.69%	Fritt (artificial Cornwall Stone)
.10	Whiting
34.00	English China Clay
8.00	English Ball Clay
14.17	Rock Flint
99.96	

These bodies were carefully ground and made up into test pieces and fired under normal and reducing conditions.

Results of Normal Burn.

The two bodies are practically equal so far as vitrification is concerned.

Regarding color the Cornwall stone body ("P") leans slightly to a brownish cream, while the fritt body ("Q") has a slight tendency toward the blue. When compared with K-3, L-3, M-3 and N-3, which have the same formulæ and which have been burned under exactly the same conditions, I find that neither the "P" nor the "Q" Body shows as much color as these bodies under normal burn. The thought could perhaps be better expressed by saying that both the "P" and the "Q" bodies show more tendency toward blue under a normal fire than do the raw bodies. Of the two when placed side by side the "Q" body shows decidedly the best color, in my judgment.

Results of Reducing Burn.

I now proceeded to fire a series of these test pieces under reducing fire and the results are as follows:

Regarding vitrification we have here an interesting study. The Cornwall stone body "P" shows a creamy translucency common to all American chinas, while the fritt body has that peculiar blue-white translucency noted in the highest types of French chinas. This is not due to over-vitrification, as neither body shows any evidence of being over-matured and neither body has warped or sagged in the firing.

Regarding color I should say that the fritt body has decidedly the preference since its color is clear, while the Cornwall stone body shows a slight but unmistakable leaning toward the brown. This is noted, however, that under reducing conditions neither of these bodies shows the blue tendency displayed by the raw bodies K-3, L-3, M-3 and N-3.

Regarding Cornwall stone as a substitute for spar, I can only say that it shows a leaning to a brown tint, similar to that produced by an excess of ball clay, and for this reason I presume would meet with discouragement. However, it must be said for Cornwall stone that it does not show the amount of variation in color that the feldspar-lime raw bodies display. However, it shows an inferior color under both normal and reducing burn to that obtained by the spar-fritt body designated as "Q." The most fruitful result of these experiments is, to my mind, the possible field of promise indicated by the developments in a spar-fritt flux for porcelain, as here we find the best color in every case, and a degree of translucency that I have never seen in American china except where overfired.

DISCUSSION.

Mr. Stover: I am very glad this paper has been read, for it simply carries out a thought I had and have not had a chance to work out, the question of using Cornwall stone as nature's own fritt; and Mr. Watts has apparently succeeded in getting a better color by making an artificial fritt. I have seen some experiments along this line come straighter than when the raw material was put in.

Mr. Mayer: Last year I visited the south of England, down in Cornwall, in an investigation of clays and Cornish stones, and I brought back samples of the best Cornish stone I could get hold of. I think I can verify what Mr. Watts has stated, that we can never get the color out of the best Cornwall stone that we can get out of the best feldspars. That may seem strange to some. We know the beautiful color of English bone china, and they are de-

pendent on Cornwall stone, some rather inferior qualities, too. But they have a condition there we do not have here; they have the bone, phosphate of lime, and the action of the lime bleaches the iron in the body. This is the only way I can account for it. There is one thing about Cornwall stone which is not generally appreciated, and that is it is one of the most variable things we can get hold of. English manufacturers appreciate that, and you must be very careful what Cornwall stone you are talking about. You may get some of the best and whitest stone to be had, and it is out of the question in comparison with the best feldspar in color. As far as vitrification is concerned, in trials of bodies using Cornwall stone for feldspar, I have had good fusion in feldspar and well marked absorption with Cornwall stone where the trials have been fired together in the biscuit kiln. English manufacturers following American methods have to get their fluxes from Sweden, in their effort to meet competition with American vitreous ware. Much of it that is exported as "vitreous" is not anything more than our ordinary well fired earthenware.

Mr. Weelans: I confess to not having had much experience in using stone in bodies. I did try it once and had such experience that I did not go further in the way of investigation; in other words, I had a blistering effect. I was just trying to use Cornwall stone in bodies in an experimental way as a substitute for spar, and noticing this blistering effect, I dropped it immediately. So, what I would have to say about the use of stone would not be very much.

Mr. Langenbeck: Mr. President and gentlemen. Of course Mr. Watts has given analyses of his Cornwall stone, but I think it would be desirable also, particularly in view of its very variable form as brought out by Mr. Mayer, that he should have mentioned something about the quality, for the benefit of those who would like to duplicate his experiments and make further application of them. Now, it is a curious fact, but nevertheless it is a fact, that potters work their heads a great deal about the raw materials, yet they

practically never go to the mills where the raw materials are ground or to the mines where they are gotten out. There is a great deal that happens in the first stages of preparing the raw material for the market that the potter ought to know. It would save trouble if he would see what is being done at the institutions preparing the materials which go into his ware. If any of you will go to the yards of Golding & Sons in Trenton, you will find a so-called "dark purple" Cornwall stone and "light buff." The purple is a hard crystalline rock. It has a purplish cast on account of large crystals of feldspathic material, and the light buff has been very considerably weathered. I should take it that the water has infiltrated through it in fine fissures and kaolinized the surface; and analyses show difference in the alkalies and possibly other ingredients.

A thing not to be left out of consideration is the fact that Cornish stone always contains fluorine; and perhaps Mr. Watts' idea of using calcium fluoride as a flux in this particular case was done because of that fact. But still that would probably introduce more fluorine and what the fluorine in the native stone and larger amounts does in firing, we do not know. Perhaps the blistering which Mr. Weelans spoke of might have been a case in which there was, through favorable conditions in the fire, disengagement of that gas on reaching a certain temperature.

I may mention one other fact in connection with Cornwall stone that may be interesting to some, as it was of quite a little commercial interest to me, at one time. That is, a vitreous body made with Cornwall stone does not shrink as much as a vitreous body made with feldspar. There might be nearly as much shrinkage and not be noticeable in the ordinary dish ware; but my use was in the making of tile, with a fireclay body and vitreous surface. If we made a vitreous body of Cornwall stone by itself its shrinkage would not be as great as one of feldspar, nor as small as the fireclay,—lying between the two. Yet if the surface of vitreous material of Cornwall stone is spread upon the rough fireclay, the moisture and the drying conditions care-

fully followed, you can get a straight tile with such a vitreous surface, while one of feldspar tile, dish. I hope this experience which does not directly bear upon the points here discussed, may be of benefit and interest to some of you.

One thing I will ask Mr. Watts, also Dr. Zimmer: why is it that American porcelain is yellowish in tone and the European porcelain is bluish?

Mr. Watts: I do not believe I would dare to offer an opinion on that, Mr. Langenbeck. I know it to be a fact, so far as my observation goes. It struck me as a peculiar fact that this artificial Cornwall stone, after being melted had a very different color and very different appearance from fritts I have made, hard fired fritts, without any fluorspar in them. The reason I used this fluorspar was just as you suggested. In a number of tests I made with different Cornwall stones, and in which I will say I found out just what Mr. Mayer said, i. e. that I could not get any two samples that would run anything near alike; and in every sample I found some trace of fluorine on testing, or at least some indication that there might be fluorine. So I used this calcium fluoride in this fritt for that reason. But after the artificial fritt was made up, I could not get any fluorine test of any kind from the artificial fritt. And, in fact, I am not surprised at that, because after it was melted, and boiling as it did, the fluorine was undoubtedly evolved. But this Cornwall stone, which I always understood the English used in their bodies, does not produce a white color. It is a decided yellow color, and I supposed it was the fluorine in the material that possibly produced it. In this case this fritt gives that color (indicating) and the Cornwall stone body of the same composition does not. So I am at a loss to know what it is. I was talking with Mr. Mayer as to the proposition of melting the feldspar, trying the refired spar alone, and I think I shall make some trials along that line to see what will be the results without adding any other material, using the refired spar against the raw spar.

Dr. Zimmer: I would like to ask Mr. Langenbeck what he means by American porcelain? Does he refer to the common china found on the American market, which actually is semi-porcelain, or does he mean bone china?

Mr. Langenbeck: The question is well taken. What I had reference to was, of course, the translucent vitreous body made here, with lead glaze, in comparison with the continental true porcelain.

Dr. Zimmer: In answer to that question, I would give two reasons why our American porcelain has to have the yellowish cast. The first reason why we have never been able to obtain such good color, is the use of plastic ball clays in the bodies, even if there is only a small percentage of it. The second reason is, that if you have a glaze containing lead, you fire with a neutral, if not an oxidizing flame and even if you have a biscuit with a grayish blue color, which is not too hard, you may obtain a glazed body with the yellowish tint, on account of the lead glaze and the conditions which must prevail in the kiln.

No manufacturer of the true hard-fired, translucent feldspar-porcelain on the continent thinks of applying stone in his porcelain body. There are certain deposits similar to Cornwall stone to be found even in Germany; but I made experiments and came to the same conclusion Mr. Watts did. However, if I want to get a strong body, i. e., for instance a body as required for sanitary ware, then I would give preference to the stone; but we must be careful and watch the composition of the stone itself.

Mr. Langenbeck: Mr. President, will you pardon a rejoinder? I suspect the difference between the two conditions, the two porcelains, is as Dr. Zimmer has indicated; but I want to make it stronger. I know nothing about the making of hard porcelain except as I have picked it up, but I understand that in the making of true, hard porcelain with a feldspar glaze, they virtually finish with a reducing atmosphere at the close of the fire. Is that so?

Dr. Zimmer: Yes, sir.

Mr. Langenbeck: Therefore you have always a fer-

rous silicate imparting little color, while in the American body, even if before glazing it may have been burned in a neutral or reducing flame, you are bound to have strongly coloring ferric oxide at the end.

Dr. Zimmer: In firing porcelain, there are certain periods when the kiln is filled with a dense smoke and fine particles of carbon are deposited in the still porous body, then you have to give a little air; otherwise, you get the bluish or rather grayish tint in the porcelain. If you would fire with smoke all along you would not get a good color either.

Mr. Binns: Before I speak of Cornwall stone, I will ask a question of Mr. Watts. I did not get it quite clear in my mind what his purpose was in making that artificial stone. What was the object in view?

Mr. Watts: I do not know, Professor Binns, but what this is going to result in an argument. I believe you yourself brought up the subject a year ago, or possibly two years ago, in a discussion with me, criticising the fact that you could not compare my results because you said I had in one case a lot of free, raw material, and on account of the increased alkalies being admitted by the spar. Do you recollect it? I determined this time my investigation should not be thus subject to Professor Binns' criticism that he was not able to compare on account of the raw materials. So in this instance, the amount of raw clay is identically the same, the free flint is identically the same, and the Cornwall stone is actually replaced by American materials fritted together so they have lost their plastic or independent qualities, so far as possible.

Mr. Binns: The reply is quite satisfactory. Mr. Watts has shown why he took the step and it is entirely reasonable. He speaks of a test for fluorine; what was this test?

Mr. Watts: Simply a quantitative test.

Mr. Binns: You tested the Cornwall stone in the raw state?

Mr. Watts: Yes, sir.

Mr. Binns: Did you after calcining?

Mr. Watts: No, I did not.

Mr. Binns: You tested the fritt after it was burned but did not get any reaction for fluorine?

Mr. Watts: Yes, sir.

Mr. Binns: With regard to Mr. Langenbeck's suggestion that there was a certain proportion of fluorspar in Cornwall stone, I think it is undoubted, and I think possibly some of that purplish color was due to the presence of fluorite. I have seen analyses as high as 1.6% of fluorspar, so the influence there would be quite marked. In regard to the composition of the stone, I have had analyses in which the alkaline content ranged from three to seven per cent. The formula of Mr. Watts would be called a fusible stone.

The spar used seemed a remarkably pure specimen. I had an interesting experience in the use of Cornwall stone in an endeavor to produce vitreous ware. It was made from Cornwall stone and the method of placing it in the glost in order to economize room, was to place the pieces on edge on protected bars, thus leaving two rough places on the edge which were polished afterwards. It was a most expensive operation, but there was no other way to get what we wanted. It happened if the plates got the least bit of a pinch of fire on the edge, a vesicular structure was produced, and that meant bubbles which prevented this polishing. The polishing would break the pimples and thus give a honeycomb surface on the edge. So we had to be extremely careful as to the point of maturity of this Cornwall stone body. I attribute that phenomenon now to the escape of fluorine. We constructed another body, using feldspar instead of Cornwall stone, and we got several curious phenomena. The ware ceased to blister, which was a good point. In the second place, the feldspar body was quite a good deal smaller, as Mr. Langenbeck has already pointed out. In the third place, it was a good deal weaker as regards the structure after burning. The plates would not stand the shock afterwards that the Cornwall stone

body would. It was a matter of pride with us that our ware would smash anything on the market, as every manufacturer claims for his ware—and it does, until it is tried by the other fellow. The Cornwall stone plate would beat the feldspar plate every time. Fourth, the feldspar plates buckled in the glost kiln very frequently. The edge upon which the plate stood would be bent. Those were some of the features we found in substituting feldspar for Cornwall stone. We had blistering with Cornwall stone, and on the other hand with feldspar we had a weaker body and greater shrinkage. One more point developed which finally made us conclude to keep up the feldspar body. The feldspar body was less liable to spit out in the decorating kiln than the Cornwall stone body, a very important point when you come to underglaze printing with gold edge.

This discussion has taken the line of the difference between American china and continental or European porcelain. I want to differ with Dr. Zimmer on one point. It is a dangerous thing to do, I know, but I am going to do it nevertheless. He said, or at least I so understood him, that even if the American biscuit were fired in a reducing fire to produce the blue tint, when the lead glaze is put on and fired in an oxidizing glost fire, the blue color will be lost.

Dr. Zimmer: I said, *might* be lost.

Mr. Binns: I am glad to have that explanation, as it is not so. It never goes yellow again. There is a maxim, I think in the burning of porcelain, that the first fire must not be higher than cone 06, because if it goes higher and the color is fixed in an oxidizing fire, it cannot be reduced. I think that is a fact. The blue-white color is undoubtedly due to the reduction of the iron oxide, as has already been pointed out.

Mr. Watts: Pardon my speaking again since this point has been brought out. I did not have the courage to contradict Dr. Zimmer, but as Professor Binns has done so, I will back him up, as the saying goes. I have in my pocket two pieces of porcelain. One I fired myself under reducing conditions, or slightly reducing conditions, and

that was sent to one of our brothers and glazed by him and finished in his kiln. He made a second body of practically the same materials, and he came back to me and said he could not get anything like the color I got with the materials. It showed nicely the fact stated, as he finished his kiln in a reasonably oxidizing atmosphere, I assume, while I finished in a reducing atmosphere. The two glazes were identically the same, and the glost kiln process identically the same in each case; and you can see by comparison of these (indicating) that the color of the biscuit kiln has not been lost. It seemed very peculiar to me when I received this trial from him that the color should be so pronouncedly yellow, whereas I never had any trouble with yellow color after it was finished in the biscuit kiln with reducing fire.

Dr. Zimmer: The whole trouble is over that little word "might." Under certain conditions you get a perfectly dense body; then you have a body so close that your oxidizing flame can't have any more influence on the body. If the bihcuit is not fired up to such a density, the condition of the kiln will have an influence and the ferrous oxide you have might be oxidized again. Besides, the color of the lead glaze is always a little bit yellowish. If you have a hard, close body, you can't expect the flame to have much influence. I forgot to mention the special conditions.

Mr. Binns: Dr. Zimmer said, as a result of reduction ferrous oxide was formed. That is not true. What is formed is ferrous silicate.

Mr. Purdy: I would like to ask Mr. Binns a question: How do you know it is ferrous silicate?

Mr. Binns: (After considerable hesitation) I don't know. (Laughter.) I can only say the evidence points that way. (Renewed laughter.)

Mr. Langenbeck: Except the evidence of variation in color afterwards.

Mr. Purdy: Take two clays which have the same iron content, one non-plastic kaolin and the other plastic ball clay. When fluxed with the same amount of feldspar a very considerable difference in color will be obtained. The

feldspar-kaolin combination invariably burns to a very peculiar white, known as Parian white, while the feldspar ball clay gives the ordinary porcelain or blue color, notwithstanding the fact that the two clays may have same iron content. A fire clay having the same iron content as our given white clays will have a very decided buff color when burned in oxidizing fire and will blue stone by mere increase in heat treatment with either oxidizing or reducing conditions. The color in each case is very different. Now, is the absolute whiteness in the first, yellowish or blue in the second, and decided buff or bluestone in the third case, due to state of oxidation of the iron or, as Seger told us, to the increased density of the iron oxide without change in state of oxidation?

Professor Binns spoke of the spar body blistering where the stone body did not—

Mr. Binns: No; it was the other way round.

Mr. Purdy: I was going to say that was at variance with Mr. Weelans' observation. But I would like to have Mr. Binns straighten us out on the iron.

Mr. Watts: Pardon me for speaking again, but I want to maintain the statement I made concerning bluestoning in the biscuit kiln. I would like to have some practical porcelain man, some one who has had some experience in vitreous American china, to contradict me if he has ever seen an instance which would justify him in contradicting me, where he got thorough bluestoning in the biscuit kiln and cleared it up in the glost. In the first place, you all know the biscuit goes three or four cones higher than the glost; and I do not believe you can vitrify and reduce a clay at cone ten and re-oxidize it at cone six. I have never succeeded in doing so; and the fact has come out in several discussions lately that you can obtain a degree of vitrification at considerably lower temperature under reducing conditions than under oxidizing conditions. So this cone ten under reducing conditions we might say is undoubtedly equivalent to at least cone twelve under oxidizing conditions, so far as vitrification or density is concerned. So we

have at least five, and probably seven cones difference, if we are going to reoxidize a reduced piece of ware in the glost kiln. I do not believe it can be done.

Mr. Binns: You will stop us, Mr. President, when you get ready. This discussion, like the snowball, gathers as it goes. I will take the first point first—Mr. Watts' statement as to the additional effect of a reducing fire.

The point made by Mr. Langenbeck as to the different colors is easily accounted for by the fact that in burning the biscuit we do not expose the pieces to the full action of the fire as a general rule. The surface of the plates is more or less protected, and for this reason the chemical action of the kiln has a less chance to get to the body than in the case of continental glazed ware, which is entirely exposed and left to the free action of the kiln gases. The plates vary very much in color if reduction be attempted, and the potter would rather have all yellow than part yellow and part blue.

Professor Purdy challenged me to prove the existence of ferrous silicate. Of course I am not able to do it, any more than he is able to prove it does not exist. The point raised as to the depth and appearance of the clay in the spar body was pointed out by me some years ago, in a paper on grinding of materials. I there showed that the body was exactly as he said—you could see right into it. But now, he is comparing the action of a ball clay mix with that of a kaolin mix. You want to compare the action of the mix under oxidizing and the same under a reducing fire. Of course there are a number of other factors that come in in influencing color, whether prepared under oxidizing or reducing conditions. Nevertheless, I believe it to be true that the ferrous silicate fuses and becomes a glass whereas the ferric oxide may remain in partial solution or free condition and causes the yellow color of the body.

Mr. Hope: I will ask whether he means with or without cobalt stain when he speaks of bluestoning. There is liable to be a confusion of two things.

Mr. Watts: In no experiment I have made for the

purpose of bringing out the color, have I introduced any stain; because if you introduce a stain you thwart the purpose of your research; you make your body an artificial blue. The bluestoning effect I called bluestoning because that is the name commonly used for buff ware when it has been reduced and turned to a bluish white cast. I have always been taught to understand and believe that it is purely the result of reducing conditions. I never heard that the blue of cobalt was intensified by reducing conditions.

Mr. Hope: But it is intensified by higher temperature.

Mr. Watts: I have never had any experience that would enable me to make any statement as to that. I never considered the use of any stain in any experiments I have made for color. That is a thing to be added after the ware is all made, and you are ready to operate, for the purpose of neutralizing any slight chrome tint that may exist.

Mr. Burt: In speaking of bluestoning there is one factor that has not been mentioned to any great extent, though Dr. Zimmer spoke of it, and that is the deposit of carbon in the pores before vitrification takes place. It is a question whether this is not one of the main problems here. Dr. Zimmer called attention to the necessity of being careful to have an oxidizing fire after the reducing fire to free the pores of the clay, before vitrification sets in, of all small particles of carbon which may be deposited there. If this is not done then you will have bluestoning that no amount of after-firing will free it from. Isn't that largely what you have there?

Mr. Watts: I will say that I have never undertaken to produce reducing conditions until after a red heat has been reached. I cannot see any advantage in doing it earlier, as it gives exactly the condition which Dr. Zimmer and Mr. Burt referred to, the tendency to precipitate carbon on the ware, which will certainly give you the grimy effect. I cannot see the advantage of maintaining reducing conditions at any time in the kiln, until after a good, bright

cherry red has been reached; and when we have reached that heat we do not have to worry about the precipitation of carbon in the ware. At least, that is my judgment. Am I right, Dr. Zimmer?

THE COMPOUNDING OF FRITS.

BY

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There are many members of the American Ceramic Society who have more or less to do with the compounding of frits and are therefore familiar with their successful manipulation. Yet in the various volumes of the Transactions are many instances of experimental work in which the compounding of frits used was based on erroneous assumptions. This leads to a two-fold evil; it detracts from the value of the work of the experimentor and, if no correction is made, may lead others of little experience into a like mistake.

The following remarks are based on the experience of the writer and on what he has been able to glean from the work of others corroborating his own work. It is not claimed that the rules laid down are final and conclusive, but they have at least the merit of having proven a reliable guide in actual practice.

The most common and most disastrous fallacy in the compounding of frits is the assumption that frits of like stoichiometrical formulæ will have like pyrometrical and physical properties. It is pretty generally admitted that the mineralogical origin and physical condition of the ingredients of a raw glaze will have a decided bearing on its character, but very often we find no such allowance made in compounding frits. It seems to be assumed that the more or less pyro-chemical work performed in the fritting operation has obliterated any differences arising from different origins and physical properties of the same chemical elements. The error is greatest when the frit is not of proper composition and is merely sintered in saggers, is slightly less when continuous fritting is employed, is still grave when the frit is brought to full fluidity and quietude in a periodic frit kiln.

On several different occasions the author has melted to full fluidity in a frit kiln mixtures having the same chemical formula but varying slightly in the origin of some of the ingredients. On applying these, either pure or mixed, with the same raw material to the same body he found, at first to his surprise, that they did not give the same results. Now he would be surprised if they did. By simply varying the selection of chemicals the same formula may be made to give a nice clear glass at a low temperature or an opaque porcelain-like mass at from 150 to 200 degrees Centigrade higher. At any point between these two extremes the mixture can be made to craze, fit or chip on any given body.

It may be of interest to know how, in the author's opinion at least, the selection of the various elements affects the character of the glass.

Feldspar.

Feldspar is taken as the foundation of the frit. It is Nature's own frit, more fusible than any chemically equivalent combination of alkali, alumina and silica compounded by man. A feldspar frit gives a more uniform and more workable glass than any other kind, and at the present price of chemicals it is also the cheapest. A Cornish Stone frit would probably be as good but would cost a little more. Frits containing a large percentage of glass sand or potter's flint, sometimes with an addition of clay, were formerly used in the enameled iron business but have been superseded by feldspar frits, with a marked improvement in the product and a decided reduction in the cost per pound of the glass. A like change might be made in other branches of the industry with similar benefits.

The selection of the spar used is of importance. Soda and soda-lime spars are more fusible than the potash, and potash-soda series, and are therefore cheaper, as they do not require such a large percentage of the expensive fluxes to produce a fusible glass. The potash spars are claimed

by some to give a glass more resistant to wear and less soluble, but this can be controlled by other factors in the composition. In selecting a spar it is necessary to make empiric tests of the brands available. This is best done by incorporating samples in frits of the same general make-up as the class to be manufactured. The spar that is most fusible by itself may not give the most fusible frit. The ultimate analysis of a spar is of little value, as the same analysis may be made up of a great variety of combinations of a number of possible minerals. This is one way that a ceramist working a stoichiometrical formula and using two or more spars indiscriminately may fail to get consistent results. There is also a physical difference in spars owing to a variation in fineness of grinding, as well brought out by Prof. Binns (Trans A. C. S., Vol. V, page 281). If we were to group all the alkali-bearing minerals together under the heading of feldspathic material and then, by a mineralogical analysis, determine feldspathic material, clay and free silica and, by a mechanical analysis, determine the physical state of the minerals present, we might have a basis for comparison of different spars. Such a method would be tedious and unconvincing and in practical work we shall probably depend, for a long time at least, on empiric tests. It is possible to substitute one spar for another according to chemical formulæ only after we have, by thorough trial in the class of work in hand, established their equivalence or obtained a factor of allowance to be made.

As has been said, spar is looked upon as the foundation of the frit; it is used in the largest amount. In general, the problem is how to reduce the melting point of spar and to alter its properties to suit our needs. Spar is a refractory element of the frit owing to its content of Al_2O_3 and SiO_2, an increase in either of these two elements causing a rise in fusing point in a normally compounded boro-silicate frit. Seldom, if ever, is it necessary to bring in these elements through other vehicles. On the one hand devitrification phenomena, incident to abnormally high

silica, and on the other hand easy solubility, if high alkalies are present, and excessive running of the glaze, incident to abnormally low Al_2O_3, are avoided by introducing them together.

Clay.

Clay is a possible source of Al_2O_3 and SiO_2. Its use is to be avoided as it impairs the fusibility to an excessive degree, making it necessary to use large quantities of expensive fluxes to produce a fusible frit. Nothing is accomplished by introducing alumina and silica in this way that can not be reached by bringing them in by means of spar, and the disadvantage is great. Mixtures overburdened with lime that are softened by the introduction of clay have no place in this class of work. High lime is permissible in raw glazes on account of the small number of fluxes available, but in the broader and richer field of fritted glazes it is to be avoided.

Flint and Sand.

These have the same effect as SiO_2 in spar but run up the fusibility much more rapidly. Physical differences have a marked effect, coarse glass sand being much more noticeable in its action than potter's flint, but if this same sand is ground as fine as the flint their action is the same. Of course they can be used in a frit but are best avoided on account of their decided hardening tendency, danger of causing devitrification, the brittle character they impart to a glaze, etc.

Aluminum Oxide.

This is one of the most refractory materials that can be added to a soft frit. It is taken into solution with great difficulty, and if added in large amounts will turn a nice fusible glass into a porcelain like mass. Free Al_2O_3 in a formula is not to be compared to Al_2O_3 from spar.

Cryolite.

The Al_2O_3 and sodium brought in through this mineral have the same effect as they do when brought in by spar. The fluorine has the same effect as in other fluroides.

The Alkalies.

From whatever source they are derived—spar, the carbonates, the nitrates, borax, etc.—the alkalies seem to always have the same effect, always making the mix more fusible. This uniformity of effect is probably due to the fact that the alkalies are either in combination, as in feldspar, or are readily fusible in themselves, if free, and so readily taken into combination.

Calcium, Magnesium and Barium Oxides.

As fluorides.—When brought in as fluorides these oxides have the same effect as if they were introduced through spar. The fluorine has its own characteristic action.

As carbonates or free.—When introduced in this form, these fluxes are less readily taken into combination and their fluxing power is lessened, especially in low temperature work. The difference is noticeable not only in the frit kiln, but in the melting of the glaze of enamel on the ware. Calcium and magnesium oxides are the most noticeable in this respect, barium oxide seeming to exert its great fluxing power with more uniformity.

Zinc and Lead Oxides.

The metallic oxides are generally added as one of the various oxides or as carbonates. There is no noticeable difference due to the elements being brought in through these two channels.

Fluorine.

Florine is used in low temperature frit work, especially where opacity is desired. It is introduced through cryolite, calcium fluoride, barium fluoride, sodium fluoride, etc. All are readily taken into solution, and there is no difference due to the various means by which the element is brought in. The effect of fluorine is always the same. It tends to reduce the melting point, to cause crazing, a milky opacity and a very fluid frit.

Boric Acid.

Boric acid is introduced by means of borax and as flaky acid. It has the same effect when brought in through either channel.

These scattered statements may be gathered together under one main proposition and a few corolaries.

1. The greater the ease with which an element is taken into solution the lower the melting point of the mixture.

That is, the fluxes exert their power more fully and the refractory elements have a less hardening effect.

a. Readily fusible minerals are taken into solution with greatest ease.

b. Elements introduced through a mineral, all of whose members are suitable to enter into combination, are taken up much more readily than if introduced alone or in combination with an inert element.

c. The finer the particles of a mineral the more readily it is taken up.

Proportioning the Frit.

The usual reason given for fritting is to produce an easily fusible glass or glaze without the use of high lead. The usual objection given against fritting is the increased cost on account of the use of more expensive ingredients and the extra labor. By a proper proportioning of the

ingredients the object mentioned can be readily obtained and at the same time a saving effected in the cost of the ware. This economy is obtained in the following ways:

1. By the use of spar as the refractory element of the glass instead of flint and clay, as in raw glazes, where high spar must be avoided on account of physical behavior in drying and burning. Being much less refractory than these other minerals spar can be used up to almost twice the weight required of them to make a suitable glaze. Only enough clay need be added in some cases to give the glass good floative qualities. In substituting potash-spar for flint in a frit formula, the practice of the writer is to use about sixteen pounds of spar in place of ten pounds of flint. In a batch where the flint, or flint and clay, thus replaced, amounts to from 40 to 60%, the saving is quite large.

2. By the use of high alkalies and consequent reduction in the amount of expensive fluxes needed. This can be safely done without danger of producing an easily soluble glass on account of the high alumina brought in by spar. As a general statement it may be said that it is safe to have the equivalent amount of total alkalies equal to the equivalent of alumina in the final glaze. In a high-spar fritted glaze this may run up to four-tenths of an equivalent, or even a little more. It is not at all necessary for all the alkalies, outside of the amount brought in by spar, to come in through borax. In fact, by substituting soluble salts of the alkalies for lime it is often possible to reduce the amount of boric acid needed to produce a fusible glass of proper coefficient. Soda-ash at a cent a pound is a cheap glaze flux.

3. By saving fuel, time and labor in the glost kiln, enameling furnace or in whatever place the frit is glazed upon a body. When the body is fully prepared in a separate operation as white ware biscuit, cast iron for enameling, etc., the advantage of a suitable coat, maturing at a considerable lower temperature than would be possible with a raw glaze, is quite great. If the body is fairly dense and uniform, it is remarkable at what low temperatures a glaze

free from crazing can be produced. Even for one-fire ware the material cost can be kept below that of a raw lead glaze and, if made in large quantities, the labor cost is not large.

Alkalies. As stated above, these are kept as high as possible without injuring the quality of the glass.

Alkaline earths, calcium and magnesium oxides. These are kept low unless introduced through spar. When added as carbonates they do not go into solution readily and are not efficient fluxes.

Metallic oxides—zinc and lead. Since lime is kept low zinc can be used to considerable extent without danger of stiffening the glaze. Pound for pound it seems to be equal or superior to lead as a flux and, as it costs less, there is economy in its use. The amount of lead used depends upon the fusibility of the glass desired and the price of borax. In nearly all cases it can be kept from exceeding .25 equivalents.

Al_2O_3 and SiO_2. As outlined above, these are for the most part brought in together by means of spar. They must be used in large enough quantity to insure a good stable glass. The experience of the writer agrees with that of Messrs. Purdy and Krehbiel (Trans. A. C. S., Vol. 9, "Fritted Glazes") in finding that alumina decreases crazing and raises the firing point, but has not found this action confined to amounts above .25 equivalents, as they state, but taking place whatever the original content of alumina.

Boric acid. Considerable has been written about the function of B_2O_3 in a glaze. Seger's statement that it decreased crazing and at the same time acted as a flux was at one time generally accepted. This is now known to be a mistake (Burt Trans. A. C. S., Vol. VII, "Coefficient Equivalents," Purdy and Krehbeil Trans. A. C. S., Vol. XIX "Fritted Glazes"). Relieved of this seeming inconsistency, we can now say that any variation, physical or chemical, that increases the fusibility of a glaze tends to increase crazing. The writer's practice has been to treat

B_2O_3 as an available flux in addition to the regular basic fluxes, but to be used as sparingly as possible on account of its high cost. The glass is to be made as fusible as possible, as indicated above, by keeping the alkalies high, the lime low, the metallic oxides fairly well up and bringing in, when possible through spar, only enough alumina and silica to produce an insoluble glass. If the glaze is still too refractory after all these things have been done, boric acid is brought in as a last resort. The introduction of B_2O_3 does not increase the solubility of the glaze to the extent that a farther increase in alkalies would and does not give the yellow color that high lead would. Otherwise boric acid can be considered equal, qualitatively, in its fluxing action to the clear glass-forming basic fluxes. By careful compounding of the rest of the glaze the amount necessary can be kept quite low. The statements that have been made to the effect that the equivalent amount of B_2O_3 must bear a certain relation to the equivalent amount of SiO_2 were no doubt true for the formulas used, but the restriction arose from other factors in the make up of the glaze, not from any necessary relation between silica and boric acid. When we call to mind that in many such cases it is possible to make an equivalent glaze without the use of boric acid at all, we know that this must be true.

Devitrification.

Devitrification has come to mean not only the crystalization of elements formerly in solution, especially frequent in very silicious glazes, but also the stone-like effect produced by the failure of some element to go into solution. These are considered to be only separate phases of the one problem of solution. In one case there is failure to dissolve and in the other is failure to hold in solution. The glaze seems to vary in its power to dissolve various elements, the alkalies, boric acid and lead oxide being dissolved in unlimited amounts, the alkaline earths, zinc and alumina sparingly, silica to a large amount. The exact limit of

solubility for any one element will depend on the amounts of the other elements present, their physical condition on entering the glaze, and the heat treatment. A large amount of one or several of the sparingly soluble elements always give trouble. Silica may be added in such amounts as to be in excess, especially at low temperatures, and this excess may be overcome by the addition of one of the sparingly soluble elements as alumina or zinc. Vice versa, addition of silica will aid in the solution of an excess of any of the sparingly soluble group. Addition of any of the very soluble group, the alkalies, lead, and boric acid tends to overcome poor solution of any of the members of the other groups. This is probably the basis of the supposition that the function of B_2O_3 is to prevent devitrification and of the standard remedy for the excess of silica, consisting of a liberal dose of alumina. These remarks are in line, I believe, with the accepted teachings in regard to the formation of eutectics. The high-lime, high-silica type of glaze is especially liable to give trouble from devitrification.

Proportioning Frit and Raw Materials.

One of the chief objects in fritting is to render some soluble ingredient insoluble, and of course all of these should be included in the frit. There must also be included enough SiO_2 and Al_2O_3, zinc, lime, or lead to produce a staple glass. If there is any ingredient that is hard to bring into combination and is erratic in its action when fluxing does begin, it is well to include the bulk of it in the fritt. Any element that is liable to be injuriously affected by kiln gases should be included in the frit. Elements that would have a tendency to fuse before the rest of the glaze, and so either suffer from volatilization or start the glaze to fusing before the proper time, should go into the frit. Inert ingredients intended for opacifiers, most pigments, and in fact anything for which especially good distribution is desirable, should also be included. In the raw part anything that is especially refractory and so

liable to remain uncombined after the bulk of the glaze has matured is best avoided. Unless added for some very special reason, it is out of place in a fritted glaze. In compounding the frit it must always be kept in mind that it has to go through the frit kiln, and that a nice fluid frit that does not attack the lining of your tank too vigorously is essential to the successful operation of a frit room.

The relative bulk of frit and raw material used will depend on the heat treatment to be given the glaze. If it is desired to produce an enamel for metals that must melt down in a very few minutes, practically all of the material must be fritted. If a glaze is being made for ware that must be in kiln for a considerable length of time, a good share of the material must be raw so as to get a slow and steady fusion and a rather viscous glaze. The raw and fritted part of the glaze should not be too far apart in fusion point or the soft portion is liable to suffer severely from volatilization. When all these restrictions are observed there is very little left to chance in the division of the raw and fritted portions of a glaze.

As stated in the beginning of these remarks, the principles here put forth have been tested in the daily work of the writer. For the reason that he feels so sure of them and on account of the amount of ground that would have to be gone over, he has not prepared experimental proofs of the statements. However, if any one has doubts as to the correctness of any of the claims made, and will so inform the writer, he will gladly attempt to substantiate his views with experimental proof covering that phase of the subject.

ACTION OF CHROMIUM OXIDE IN GLAZES CONTAINING ZINC.

BY

MERRILL L. BRYAN, Columbus, Ohio.

In discussions that have come up on different occasions between several men making a specialty of glaze work and myself, the use of raw Chromium Oxide was one that seemed to have caused the most trouble, and the most talk; also the fact that the books generally used by glaze men had reference to no other material than iron, that was detrimental to production of good green colors with the raw oxide. There was evidently something else that hindered the chrome from producing the green, because in most cases iron was found to be absent.

My own experience with the use of raw chromium oxide dates back to 1905, at the plant of the Altanta Terra Cotta Company, Atlanta, Ga., when I was called upon to make a green matt glaze. The temperature was cone 3, the duration of burn several days; consequently copper oxide was out of the question, and I had to rely on the use of chromium oxide.

I had been using a white matte glaze on the terra cotta, with very good results, therefore I used it as a base for my color series. This glaze had a large content of zinc oxide, but this fact did not suggest itself to me as being a disadvantage. I made up trial glazes, using the white with addition of raw oxide of chromium from .01 to .05 equivalents. These glazes were sprayed upon the body, which had previously been coated with a white engobe, and fired to cone 3, in a down-draft muffle kiln. When the kiln was drawn, I was surprised to find that I did not have green glazes, as I expected, but instead I had several shades of brown.

I immediately concluded that iron was present, or had

been furnished in some way. Possibly the buff body had had some effect upon the glaze, even through a white engobe. One of the bodies down there was made from the native clay, and the percentage of iron in it was very small, as it burned pure white. I covered this body with the same engobe and the same glazes, and got the same results. I could not see how my glaze materials could contain sufficient iron to effect the chrome, as they were the best the market afforded.

In the meantime I had been trying to cheapen the white matte by cutting down the zinc oxide, and had at last perfected a glaze that contained no zinc oxide at all. I tried the different coloring oxides in this glaze to see what kind of colors I could produce with it, and along with the rest I put some chromium oxide. To my surprise, I got the green I wanted, but when I made it up I had no idea that the result would be different than before.

I spoke to Prof. Orton about my experience with these glazes, and he suggested that it would be a good idea to carry out a line of experiments, and read the results to the American Ceramic Society.

The first thing that was necessary was a series of matte glazes, in which the zinc oxide could be varied at the expense of some other material from zero to a large quantity, and at the same time not affect the texture of the glaze.

This series is:

No.	K_2O	CaO	BaO	ZnO	Al_2O_3	SiO_2
10	.25	.30	.45	.00	.3	2.
20	.25	.28	.42	.05	.3	2.
30	.25	.26	.39	.10	.3	2.
40	.25	.24	.36	.15	.3	2.
50	.25	.22	.33	.20	.3	2.
60	.25	.20	.30	.25	.3	2.
70	.25	.18	.27	.30	.3	2.
80	.25	.16	.24	.35	.3	2.
90	.25	.14	.21	.40	.3	2.

BATCH WEIGHTS.

No.	Spar.	Whiting.	Barium.	Zinc.	Clay.	Flint.
10	139.25	30.0	88.65	0.00	12.9	24.0
20	139.25	28.0	82.74	4.05	12.9	24.0
30	139.25	26.0	76.83	8.10	12.9	24.0
40	139.25	24.0	70.92	12.15	12.9	24.0
50	139.25	22.0	65.01	16.20	12.9	24.0
60	139.25	20.0	59.10	20.25	12.9	24.0
70	139.25	18.0	53.19	24.30	12.9	24.0
80	139.25	16.0	47.28	28.35	12.9	24.0
90	139.25	14.0	41.37	32.40	12.9	24.0

The zinc was added at the expense of the lime and barium, the ratio between these being the same throughout —2:3. These were selected because the varying of the potash would cause a difference in the amount of spar and clay to be added, consequently if iron was present in them, it would be constantly varying.

The extremes were ground in a ball mill for one hour, then evaporated to dryness in order to make the blends by dry weight.

No.	No. 10.	No. 90.	Eq. Weight.
10	All	None	294.80
20	7 Parts	1 Part	290.94
30	6 Parts	2 Parts	287.08
40	5 Parts	3 Parts	283.22
50	4 Parts	4 Parts	279.36
60	3 Parts	5 Parts	275.50
70	2 Parts	6 Parts	271.64
80	1 Part	7 Parts	267.78
90	None	All	263.92

To each of the blends made up, four additions of green oxide of chromium were made, viz:—.005, .010, .015 and .02, equivalents.

No.	.76 Cr_2O_3	No.	1.52 Cr_2O_3	No.	2.28 Cr_2O_3	No.	3.04 Cr_2O_3
11	294.80	12	294.80	13	294.80	14	294.80
21	290.94	22	290.94	23	290.94	24	290.94
31	287.08	32	287.08	33	287.08	34	287.08
41	283.22	42	283.22	43	283.22	44	283.22
51	279.36	52	279.36	53	279.36	54	279.36
61	275.50	62	275.50	63	275.50	64	275.50
71	271.64	72	271.64	73	271.64	74	271.64
81	267.78	82	267.78	83	267.78	84	267.78
91	263.92	92	263.92	93	263.92	94	263.92
	Dry Glaze		Dry Glaze		Dry Glaze		Dry Glaze

These were then ground in a ball mill for thirty minutes, gumtragacanth solution being used in order to make the glazes adhere to the tile. These were applied to bisque tile, making thirty-six samples. The firing was carried on in a gas muffle kiln, at the Ceramic Laboratory of the Ohio State University, at the temperature of cone 3.

The range of green colors was very small, as spots of brown began to show at number 33. The zinc content at this point is .1 equivalent, and the chromium .015 equivalent; from this point up, the browns become more pronounced.

TRANS. AM CER SOC VOL X BRYAN

	.00ZnO	.05ZnO	.10ZnO	.15ZnO	.20ZnO	.25ZnO	.30ZnO	.35ZnO	.40ZnO
.005 Cr_2O_3	11	21	31	41	51	61	71	81	91
.010 Cr_2O_3	12	22	32	42	52	62	72	82	92
.015 Cr_2O_3	13	23	33	43	53	63	73	83	93
.020 Cr_2O_3	14	24	34	44	54	64	74	84	94

In explaining this, my idea at first was that the zinc oxide had remained suspended in the glaze, just as it does in a Bristol glaze, only that the matte glaze is more immature, and the quantity of zinc oxide uncombined is greater. Chromium oxide is taken into a glaze with difficulty, hence, with two materials not taken into the glaze, there is a possibility that they might go together and form a chromate of zinc, but this point was in doubt, owing to the fact that one end of my kiln had a few pieces of the high zinc series, which had been exposed to the flame. These were matured, but instead of being brown, were green. To ascertain whether this was due entirely to reduction, or to the fact that most of the zinc had been taken into solution, led me to refire the trials to cone 9, in a good oxidizing fire, in order to mature them. This heat did not mature the glazes, neither did it change the color of the flashed pieces.

To get at this, it was necessary to design a new series, that could take a large quantity of zinc into solution. Lead was used as a flux to do this, and the series runs as follows:

No.	PbO	CaO	K_2O	ZnO	Al_2O_3	SiO_2
100	.50	.40	.10	.00	.15	1.5
200	.50	.35	.10	.05	.15	1.5
300	.50	.30	.10	.10	.15	1.5
400	.50	.25	.10	.15	.15	1.5
500	.50	.20	.10	.20	.15	1.5
600	.50	.15	.10	.25	.15	1.5
700	.50	.10	.10	.30	.15	1.5
800	.50	.05	.10	.35	.15	1.5
900	.50	.00	.10	.40	.15	1.5

BATCH WEIGHTS.

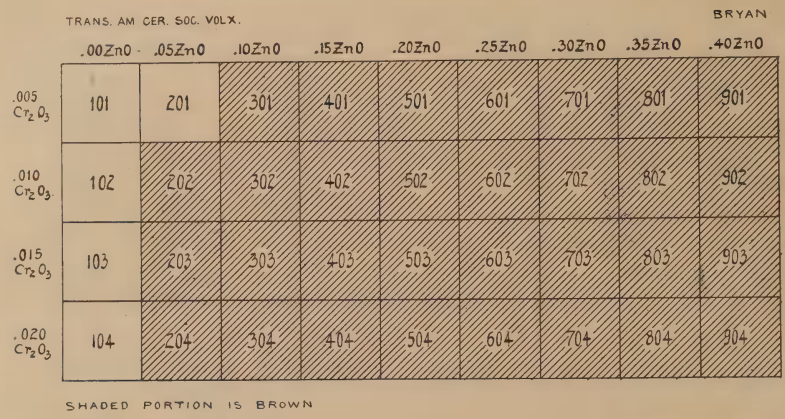
No.	Lead.	Whiting.	Spar.	Zinc.	Clay.	Flint.
100	129.00	40.00	55.70	00.00	12.90	40.00
200	129.00	35.00	55.70	4.05	12.90	40.00
300	129.00	30.00	55.70	8.10	12.90	40.00
400	129.00	25.00	55.70	12.15	12.90	40.00
500	129.00	20.00	55.70	16.20	12.90	40.00
600	129.00	15.00	55.70	20.25	12.90	40.00
700	129.00	10.00	55.70	24.30	12.90	40.00
800	129.00	5.00	55.70	28.35	12.90	40.00
900	129.00	00.00	55.70	32.40	12.90	40.00

The same treatment was given this series in preparation that was given the matte series, the trials were fired in the same kiln, to cone 1, instead of cone 3. Numbers 100 and 200 are immature; numbers 800 and 900 show crystals of zinc; numbers 300, 400, 500, 600 and 700 are good clear glazes, showing no opacity, and no crystalline segregations.

To each of the above glazes, the same amounts of chromium oxide were added, viz:—.005, .01, .015 and .02, equivalents.

No.	.76 Cr_2O_3	No.	1.52 Cr_2O_3	No.	2.28 Cr_2O_3	No.	3.04 Cr_2O_3
101	277.60	102	277.60	103	277.60	104	277.60
201	276.65	202	276.65	203	276.65	204	276.65
301	275.70	302	275.70	303	275.70	304	275.70
401	274.75	402	274.75	403	274.75	404	274.75
501	273.80	502	273.80	503	273.80	504	273.80
601	272.85	602	272.85	603	272.85	604	272.85
701	271.90	702	271.90	703	271.90	704	271.90
801	270.95	802	270.95	803	270.95	804	270.95
901	270.00	902	270.00	903	270.00	904	270.00
	Dry Glaze		Dry Glaze		Dry Glaze		Dry Glaze

The result was the same, only the green had even a smaller range, only five showing a green tint.



From these two series it can be seen that the brown colors are not due to the presence of uncombined zinc; but that the zinc is the element that is detrimental to the chromium oxide in producing its best color, there can be no doubt.

The higher forms of chromium are not greens, but are browns. The ordinary atmosphere of a kiln in my opinion, is not sufficient to oxydize the Cr_2O_3 or green oxide to a higher form, and as there is no compound of zinc between the ZnO and Zn forms, zinc oxide does not act as an oxydizing agent.

I can only see one material that this higher or acid form of chrome could attack, and that would be the zinc, the result would be the formation of a chromate of zinc, but in the color series of number 800, the surfaces of the tile are completely covered with crystals, while the clear glaze only shows them around the edges, one or two on the face. If zinc chromate were formed, zinc oxide would be taken from the glaze, consequently the glaze would be less liable to become supersaturated with zinc, consequently the tendency of crystallization would be lessened.

The conclusion I draw from this series of trials, is that the zinc oxide acts as an agent, supplying the oxygen necessary to change the Cr_2O_3 to a higher form, where it remains as such, unless it is given a violent reducing atmosphere.

The coloring power of chromium then is merely a question of oxidation, and when zinc is present the chromium is oxidized to its higher form, hence the brown color.

DISCUSSION.

Mr. Plusch: My experience corroborates Mr. Bryan's throughout. I have done similar work, using zinc oxide with different coloring oxides in glazes. I have found that the effect of the zinc oxide on the coloring oxides is extremely variable and interesting. For instance, the higher the zinc in a cobalt glaze, the more it runs to the violet, and the less zinc, the more it runs to the cold blue. Of all the bases ZnO seems to be the most active in producing interesting effects with coloring oxides.

Mr. Mayer: I have had a little experience with zinc oxide in connection with underglaze colors. At one time a firm in East Liverpool asked me to supply them with a color such as I was using for underglaze ware. I sent the color down and they sent the trial back—as fine a raven black as you could get. I asked the person who shipped it what the matter was, and he said he sent the No. 868 green, which we used. I sent another lot down myself. They were wanting to adopt a green stamp, but when the trial came back it was exactly the same, a black. Our glaze contains no oxide of zinc—we never use it in glaze, and under our glaze this color is a very brilliant green. It seems that no matter what percentage of zinc is in the glaze, it will affect the color, ranging from a black to a dirty brown. The color itself contains twenty percent of oxide of zinc. Where there is no oxide of zinc in the glaze, every time the color is a brilliant green, very stable; but

directly you get oxide of zinc in the glaze, even where it runs four or five percent, it will make it run from a brown to black.

Mr. Humphrey: In making brown matt glazes with chromium and zinc, I have noticed a variation in color due to different lengths of time burning. The color I produced on many occasions, which was a uniform brown in the ordinary burn, even though the temperature varied, if burned in the trial kiln in, say, twenty-four hours, it came out a distinct green. I don't know the reason unless the zinc did not combine with the chromium in so short a time. In pulling down the kiln door, where the brown matt glaze is exposed to view while the kiln is still very hot, the glaze is very distinctly green, but as it cools it turns to brown and does not show any green. The difference in the length of burning makes a very decided difference in the color.

Mr. Bryan: I determined that myself. I took a small muffle kiln at the University and put in some burned trials and heated it to about cone 010, then gave it violent smoking treatment and closed it up. Some pieces that I drew out red hot were a nice green when they were first pulled out and when cool went back to brown again, though not exactly the same shade of brown as before.

Mr. Humphrey: The variation in color seems to be due to variation in length of burning rather than variation in length of cooling. In a long burn it will be a distinct brown, but in a short burn it will not be, no matter how quickly it is cooled. I have also flashed it, but did not change the color materially.

NOTE ON FLINT BLOCKS vs. WOODEN BLOCKS FOR CYLINDER LININGS.

BY

H. E. Ashley, Newell, W. Va.

Flint blocks are rapidly taking the place of wooden blocks as a lining for cylinders for grinding "flint" and "spar" for pottery purposes, so that a note on the relative efficiency of the two linings will be of interest.

The Potters' Mining and Milling Co., of East Liverpool, made the change some time ago. Previous to that time they had been getting with a six hour grind a product (ground quartz sand) with about two per cent. matter that would not go through a No. 13XX silk lawn (50.4 meshes per linear centimeter, 128 meshes per linear inch).

After the change, a test was made to determine how long a grind, with all other conditions the same, was required to get a product of the same fineness. Samples were taken at the end of successive hours, and the portions weighed that were retained on brass seives of 7.9 mseshes and 31.5 meshes per linear centimeter (20 and 80 meshes per linear inch) and on No. 13XX silk lawn. The results are given in the following table:

Duration of Grinding.	RETAINED ON		
	7.9 Meshes per Cen. 20 Meshes per Inch.	31.5 Meshes per Cen. 80 Meshes per Inch.	50.4 Meshes per Cen. No. 31XX Silk Lawn.
3 hours.	.06 per cent.	2.66 per cent.	6.21 per cent.
4 "	.73 "	.02 "	1.82 "
5 "	.25 "	.20 "	.48 "
6 "	.73 "	.02 "	.14 "
Nature of Residue.	Accidental matters, fragments of flint, pebbles, etc.	Unground sand.	Coarse ground sand.

The figures show that the same results were obtained in four hours by using the flint lining that had previously been obtained in six hours with the wood lining.

The test was conducted by the superintendent, Mr. John Arnold, now deceased, the sifting and lawning was done by the writer, and the results are now communicated by permission of the president, Mr. Joseph G. Lee.

MEMORANDA ON CRUSHING STRENGTH OF TERRA COTTA.

BY

R. F. GRADY, St. Louis, Mo.

The terra cotta cubes used in the following compression tests were made by the St. Louis Terra Cotta Co.

In making these pieces three mixtures of clay were used, designated in the tables as "L.B.," "3C" and "R" prepared as follows:

"LB"	8 parts local buff clay 2 parts Indiana buff clay 4 parts grit	All thru No. 16 screen
"3C"	5 parts local buff clay 5 parts Indiana clay 4½ parts grit	All thru No. 16 screen
"R"	2½ parts local buff clay 4 parts local shale 5½ parts grit	All thru No. 16 screen

The cubes were pressed in plaster moulds and no finishing done more than necessary to remove the seams. Samples "LB" and "3C" were fired to cone 4 while samples marked "R" were fired to cone 02.

Table No. 1 shows results of tests of 12 cubes each of the three mixtures, one half of the test pieces being 2″ cubes and one half 4″ cubes. These pieces were broken without any special preparation except as noted where plaster or cement caps were used. The results shown in this table do not indicate that artificial caps increase the crushing strength of the pieces.

Table No. 2 shows the results of breaking six each of the 2″ cubes of pieces "LB," "3C"" and "R." In composition and method of manufacture these pieces are identical with

those of Table No. 1, the only difference being that two opposite faces on these blocks were rubbed smooth and approximately parallel. These smooth faces came into contact with the crushing plates with no artificial capping.

Comparing the averages of Tables 1 and 2 it appears that grinding the bearing surfaces increases the crushing strength materially.

The breaking tests on these blocks were made in the St. Louis Water Department Testing Laboratory under the direction of Mr. E. E. Wall, Asst. Water Commissioner.

CRUSHING TESTS OF TERRA COTTA.

TABLE No. 1. R. F. Grady

No.	Mark.	Size of Cube.	First Crack.	Ult. Strength.	Pounds per Square Inch.	Average Crushing Strength.	
1	LB.	2″	9,300 lbs.	20,820 lbs.	5,205		No Cap
2	LB.	2″	22,000 lbs.	22,790 lbs.	5,697		No Cap
3	LB.	2″	6,420 lbs.	19,610 lbs.	4,902	5121	No Cap
4	LB.	2″	11,400 lbs.	23,530 lbs.	5,882		No Cap
5	LB.	2″	6,700 lbs.	20,530 lbs.	5,107		No Cap
6	LB.	2″	7,480 lbs.	15,740 lbs.	3,935		No Cap
7	LB.	4″	66,000 lbs.	70,920 lbs.	4,432		No Cap
8	LB.	4″	55,800 lbs.	59,730 lbs.	3,733		Plaster Cap
9	LB.	4″	57,000 lbs.	62,470 lbs.	3,904	4288	Plaster Cap
10	LB.	4″	64,000 lbs.	84,830 lbs.	5,302		Plaster Cap
11	LB.	4″	43,000 lbs.	69,050 lbs.	4,315		Cement Cap
12	LB.	4″	37,500 lbs.	63,090 lbs.	3,943		Cement Cap
1	3C.	2″	2,210 lbs.	15,690 lbs.	3,922		No Cap
2	3C.	2″	3,610 lbs.	19,210 lbs.	4,802		No Cap
3	3C.	2″	15,000 lbs.	30,710 lbs.	7,677	6317	No Cap
4	3C.	2″	14,000 lbs.	28,060 lbs.	7,015		No Cap
5	3C.	2″	23,340 lbs.	27,020 lbs.	6,755		No Cap
6	3C.	2″	18,000 lbs.	30,930 lbs.	7,732		No Cap
7	3C.	4″	40,000 lbs.	100,000+lbs.	6,250		No Cap
8	3C.	4″	77,000 lbs.	93,480 lbs.	5,842		Plaster Cap
9	3C.	4″	76,000 lbs.	98,520 lbs.	6,157	6107	Plaster Cap
10	3C.	4″	79,000 lbs.	100,000+lbs.	6,250		Plaster Cap
11	3C.	4″	66,000 lbs.	100,000+lbs.	6,250		Cement Cap
12	3C.	4″	60,270 lbs.	94,340 lbs.	5,896		Cement Cap
1	R.	2″	5,450 lbs.	14,230 lbs.	3,557		No Cap
2	R.	2″	8,280 lbs.	14,670 lbs.	3,667		No Cap
3	R.	2″	10,200 lbs.	25,370 lbs.	6,342	4511	No Cap
4	R.	2″	12,360 lbs.	17,450 lbs.	4,362		No Cap
5	R.	2″	10,000 lbs.	22,790 lbs.	5,697		No Cap
6	R.	2″	5,000 lbs.	13,760 lbs.	3,440		No Cap
7	R.	4″	49,000 lbs.	78,480 lbs.	4,905		No Cap
8	R.	4″	62,000 lbs.	86,020 lbs.	5,376		Plaster Cap
9	R.	4″	74,190 lbs.	74,190 lbs.	4,637	4754	Plaster Cap
10	R.	4″	38,000 lbs.	65,310 lbs.	4,682		Plaster Cap
11	R.	4″	36,000 lbs.	68,980 lbs.	4,311		Cement Cap
12	R.	4″	63,000 lbs.	73,820 lbs.	4,614		Cement Cap

CRUSHING TESTS OF TERRA COTTA.

TABLE No. 2.

R. F. Grady

No.	Mark.	Size of Cube.	First Crack.	Ult. Strength.	Pounds per Square Inch.	Average Crushing Strength.	Initial Height.	Height First Crack.	Difference.	Average.	
1	LB.	2″	20,650 lbs.	21,750 lbs.	5,437						No Cap
2	LB.	2″	21,450 lbs.	27,470 lbs.	6,867		2.010 inch	1.990 inch	.020 inch		No Cap
3	LB.	2″	21,570 lbs.	23,980 lbs.	5,995	5767	2.020 inch	2.010 inch	.010 inch	013	No Cap
4	LB.	2″	14,580 lbs.	19,920 lbs.	4,980		1.925 inch	1.910 inch	.015 inch		No Cap
5	LB.	2″	10,400 lbs.	25,610 lbs.	6,402		2.015 inch	2.005 inch	.010 inch		No Cap
6	LB.	2″	13,220 lbs.	19,690 lbs.	4,922		1.995 inch	1.985 inch	.010 inch		No Cap
7	R.	2″	9,500 lbs.	23,340 lbs.	5,835		1.990 inch	1.980 inch	.010 inch		No Cap
8	R.	2″	9,920 lbs.	27,950 lbs.	6,988		2.005 inch	1.995 inch	.010 inch		No Cap
9	R.	2″	9,700 lbs.	24,830 lbs.	6,207	6428	2.015 inch	2.005 inch	.010 inch	0095	No Cap
10	R.	2″	15,350 lbs.	29,860 lbs.	7,465		1.970 inch	1.960 inch	.010 inch		No Cap
11	R.	2″	12,770 lbs.	27,650 lbs.	6,912		1.979 inch	1.974 inch	.005 inch		No Cap
12	R.	2″	17,710 lbs.	20,640 lbs.	5,160		2.018 inch	2.006 inch	.012 inch		No Cap
13	3C.	2″	29,190 lbs.	44,630 lbs.	11,158		1.962 inch	1.947 inch	.015 inch		No Cap
14	3C.	2″	19,040 lbs.	28,340 lbs.	7,085		1.974 inch	1.963 inch	.011 inch		No Cap
15	3C.	2″	25,910 lbs.	36,390 lbs.	9,098	8776	2.026 inch	2.011 inch	.015 inch	0132	No Cap
16	3C.	2″	24,470 lbs.	32,250 lbs.	8,062		2.017 inch	2.001 inch	.016 inch		No Cap
17	3C.	2″	19,660 lbs.	38,910 lbs.	9,728		1.961 inch	1.948 inch	.013 inch		No Cap
18	3C.	2″	23,670 lbs.	30,300 lbs.	7,525		1.952 inch	1.943 inch	.009 inch		No Cap

DISCUSSION.

The Chair: I think this question of the strength of terra cotta is an important one and is being constantly brought up by engineers. In these days of concrete construction, it seems appropriate that work be done along this line. I will ask Mr. Grady if he ever had tests made upon the finished blocks of his terra cotta; and whether or not the crushing strength of the finished block is proportional with the crushing strength of his cubes? Whether any weaknesses developed in the finished blocks which did not show in the cubes?

Mr. Grady: I never made any tests except in that form. That question came up very recently or I should have presented some tests along that line. I think it is very essential, as it is really the condition in which the terra cotta is brought into service that we want to know about. I have planned to make some tests along that line and hope to present them later on. It is only rarely that architects specify the crushing strength to which terra cotta must be subjected. We recently had occasion to figure on a job in which the specifications called for a crushing strength of six thousand pounds to the square inch. I did not know whether we could figure on it intelligently or not.

Mr. Stull: I will ask whether you used anything to represent the mortar joint, or whether the piece was in contact with the crushing plate?

Mr. Grady: In the tests shown on sheet number two, which I am sorry I cannot show you, in which the crushing strength runs considerably higher, the pieces were brought into direct contact with the iron plates. On the other sheet the tests shown were made without polishing the pieces. Some of them were capped with Portland cement caps and some with plaster. From these experiments I find it does not increase the strength of the piece any, and, theoretically, I believe it should diminish it.

Mr. Stull: I have tested some enameled brick, but I do

not know that any standard for testing has been established. The method I used was to place a half inch pine board above and below. I tested a solid brick which gave a crushing strength on the flat, not to the square inch, of 120 tons. We tested brick cored out with three holes which ran something like 20 tons on the flat. Our drier was not large enough and we decided to core out more holes to decrease the time of drying. We cored out brick with eleven holes and I was skeptical as to its strength, but in the hydraulic press it showed 44 tons on the flat. We decided there was a sufficient factor of safety in this figure.

ON THE DEGREE OF SUBDIVISION OF MATERIALS IN USE IN THE CERAMIC INDUSTRY.

BY

CLIFFORD RICHARDSON, New York City, New York.

In the course of extensive studies on the relation of the degree of subdivision of materials used in the production of Portland cement clinker, I have shown that this has a most important influence on the character of the clinker and of the Portland cement which is produced from it. It at once occurred to me that the same thing might have a very decided influence on the character of porcelain bodies, and, with this in view, I had a large number of thin sections made for microscopic study, of such porcelains as are available in our local markets. It was at once very evident that the raw materials of which these were composed were so coarse as to prevent any thorough diffusion between the different components in the time during which, and at the temperature at which they were burned, and at which they retain their original moulded shape.

With a view of determining what the degree of subdivision of these raw materials is as they are used in the ceramic industry, a collection was made of various flints, spars and clays available in the market. In making such a determination, sieves and bolting cloths are useless, as none of them will serve to separate the different particles of a diameter less than .06 mm. In order to differentiate such particles which form the preponderating mass of ground flint, spar and clay, it is necessary to take advantage of the fact that the finer a particle of mineral matter is, the longer will it remain suspended in water. In this way, by what is known as elutriation, the particles of flint, spar and clay can be separated into those which remain suspended in water for various periods, 15 seconds, 30 seconds, and so on. As the quantity which will remain

suspended in a definite time will vary with the purity and temperature of the water, and with the manner in which the material has been put in suspension, some definite conditions for taking the separation of the particles into different sizes in this way must be agreed upon. Such conditions were first fixed by Mr. Alen Hazen in the 24th Annual Report of the Massachusetts State Board of Health for 1892, and may be described as follows:

Five grams of the material to be examined are placed in a beaker about 120 mm. high, holding about 600 cc. The beaker is nearly filled with distilled water at a temperature of exactly 68° F. The water is then agitated with an air blast through a small opening in a glass tube until the powder and water are thoroughly mixed, taking care, by moving the glass tube from side to side, not to produce a cyclonic motion in the latter. The blast of air is then stopped and the liquid allowed to stand for exactly 15 seconds, when the water above the sediment is decanted from it without pouring off any of the latter. This washing is repeated three times. The sediment is then washed out into a dish, dried and weighed. The operation can be repeated with a new quantity of material, extending the time for sedimentation to 30 seconds, and, in the same way, for longer periods.

In this way, the flints, spars, and clays which were at hand were examined, with the results given in the following table:

DEGREE OF SUB-DIVISION OF MATERIALS IN USE IN THE CERAMIC INDUSTRY.

Test No.	IDENTIFICATION.	Residue on 200 Mesh Screen.	SETTLED AFTER		Not Settled.
			15 Sec.	30 Sec.	
	FLINT.				
94186	Flint—Trenton	0.8%	20.8%	15.0%	63.4%
94437	Flint—Trenton	3.4%	13.7%	8.2%	74.7%
94337	Flint—Baltimore	1.5%	9.1%	6.1%	83.3%
94338	Flint—Trenton	.6%	7.1%	6.6%	85.7%
94414	Flint—Chicago	.1%	3.4%	4.0%	92.5%
94731	Flint—Illinois, No. 15	.1%	16.4%	8.9%	74.6%
94732	Flint—Illinois, No. 40	2.1%	.2%	.2%	97.5%
	SPAR.				
94187	Spar—Baltimore	8.4%	23.8%	18.3%	49.5%
94188	Spar—Trenton	0.4%	10.1%	13.1%	76.4%
94436	Spar—Trenton	0.9%	6.2%	3.5%	89.4%
94339	Spar—Trenton	3.7%	10.3%	6.2%	79.8%
94583	Spar—Pennsylvania	0.5%	4.8%	7.0%	87.7%
94415	Spar—Chicago	2.8%	3.4%	3.0%	90.8%
	KAOLIN.				
94190	Kaolin—Florida	0.5%	2.5%	5.6%	91.4%
94191	Kaolin—Georgia	1.4%	3.2%	3.2%	92.2%
94192	Kaolin—Missouri	12.6*%	3.3%	3.5%	80.6%
	ENGLISH CLAY.				
94194	China Clay—English	5.6%	0.1%	0.2%	94.1%
94195	China Clay—Hockessin	3.0%	1.6%	2.7%	92.7%
94413	China Clay	3.0%	1.6%	4.2%	91.2%
	BALL CLAY.				
94196	Ball Clay—English	1.5%	6.2%	2.2%	90.1%
94197	Ball Clay—Mayfield	7.5%	0.6%	0.2%	91.7%
94198	Ball Clay—New Jersey	Trace	1.6%	2.2%	96.2%
94199	Ball Clay—Tennessee, No. 1	0.2%	6.9%	5.9%	87.0%
94200	Ball Clay—Tennessee, No. 2	0.9%	4.7%	6.3%	88.1%
94201	Ball Clay—Tennessee, No. 3	2.2%	2.5%	1.5%	93.8%

*Sand.

The preceding data are of interest as showing that while in nearly every case the flints, spars and clays are so fine as to practically all pass the finest sieve, they differ to a very decided degree in the amounts which are so fine as to remain suspended for more than 30 seconds. In the case of the ground flints, the particles of this latter size were found to vary from 63.4 to 97.4 per cent. of the entire powder, and in the case of the spars, from 49.5 to 90.8.

Such a difference in the degree of sub-division must have a very decided influence upon the character of the porcelain bodies of which they are components. The difference in the degree of sub-division in the clays is not as large, as these substances are made up of extremely fine particles produced in nature by the disintegration of rock, rather than by artificial grinding. There are, however, differences of as much as 16 per cent. in this respect, and it is one which must be taken into consideration.

The cohesion and strength of all ceramic articles after burning must be attributed to what would be designated the "sintering" together of the components. It is interesting for the moment to consider what this sintering is. From the point of view of the physical chemist, it is the diffusion of the material of which two particles are composed into each other at the point of contact, at a temperature below the point of fusion. If two gases are brought together, they diffuse into each other with great rapidity. If two liquids are poured one upon the other in layers, without mixing, they diffuse more slowly. If solids are brought into contact, it would be naturally assumed that diffusion would cease. Experiments of Roberts-Austen have shown that molecular mobility in solids exists, since when carefully polished surfaces of gold and lead are brought into contact and left under pressure for some months, at the ordinary temperatures, gold is diffused into the lead and the lead into the gold for an appreciable distance. Mixtures of the components which would produce a fusible Wood metal when subjected to pressure at ordinary temperatures, become converted into this alloy. Anhydrous sulphate of soda and cambonate of barium also diffuse when brought into close contact with the formation of barium sulphate and carbonate of soda.

It is not difficult to understand, therefore, how at the temperature at which the porcelain wares are burned, the materials of which the flint, spar and clay are composed may diffuse to such an extent as to result in an adequate cohesion on cooling. This is known as sintering. The dif-

fusion is, of course, a partial one, and not complete, as in the case of Portland cement clinker, which occurs at a much higher temperature. The diffusion on fusion, of course, would be more rapid, but this would not be permissable in the ceramic industry. Under such conditions, glass would be produced, which is a type of solid solution.

The homogeneity of a porcelain body, its fineness and general characteristics, will, of course, depend to a very considerable degree, on the extent to which diffusion has taken place. From the point of view of the physical chemist, this is dependent upon the area of the surface of the different constituents which come into contact, as shown by Fick's law.

From a study of salt solutions of different degrees of concentration, Fick determined that the amount of salt which diffuses through a given cross-section is proportional to the difference in concentration of two cross-sections lying indefinitely near to each other, or is proportional to the difference in cross-section. From this law, it will be seen that the fineness of the raw materials entering into the composition of a porcelain body will have a striking influence on its character after burning, as the area of the surface of the particles which come into contact will be dependent thereon. Some preliminary experiments made on the production of porcelain bodies from those portions of the flint, spar and clay which remain suspended in water for more than 30 seconds, showed that this reasoning was correct, as much finer bodies were obtained. It is quite possible that porcelain bodies prepared in this way, aside from their improved appearance, may show a decided improvement in their physical characteristics, especially in brittleness. Experiments carried out in this direction will be of the greatest interest. An examination of a large number of thin sections of porcelain collected in the local markets, and manufactured in England, France, Germany, and the United States, showed the greatest difference in structure under the microscope; and this structure was apparently largely due to differences in the degree of fine-

ness of the components of which these bodies were made. In many of them, particles of spar which had not lost their crystalline form or optical activity were visible, while in others, a more or less complete diffusion was evident.

The preceding data are presented with a view of pointing out a line of study which may offer results of considerable interest to ceramists.

NOTE ON DRYING OF CLAYS.

BY

EDWIN F. LINES, Champaign, Illinois.

(The experiment described below was made at the suggestion of Professor A. V. Bleininger, of the School of Ceramics, University of Illinois, to whom the author is indebted for advice as to method of operation and presentation of results.)

In order to throw, if possible, some new light on the phenomena of drying, the writer made a careful record of the periodic changes which take place during the drying of several types of clays. The types selected were shale, No. 2 fire clay, and glacial clay.

The experiment was carried out briefly as follows: Each of the samples, with the exception of one of the No. 2 fire clays, which had been washed before it reached the laboratory, was sifted through a 12 mesh screen and mixed with enough water to make it work easily. After each sample had been thoroughly wedged it was pressed in plaster moulds into two spheres 6 and 7 centimeters in diameter. The spheres were then placed in a damp closet over night so as to establish conditions of equilibrium. They were then dried in a gas-heated laboratory drying oven, the temperature of which was kept constant by means of a mercury thermostat. The progress of the drying was recorded from half-hourly weighings and measurements. The measurements were made with vernier calipers reading to .1 mm., and the diameter of the sphere determined from the average of four measurements taken upon axes fixed by marks on the surface.

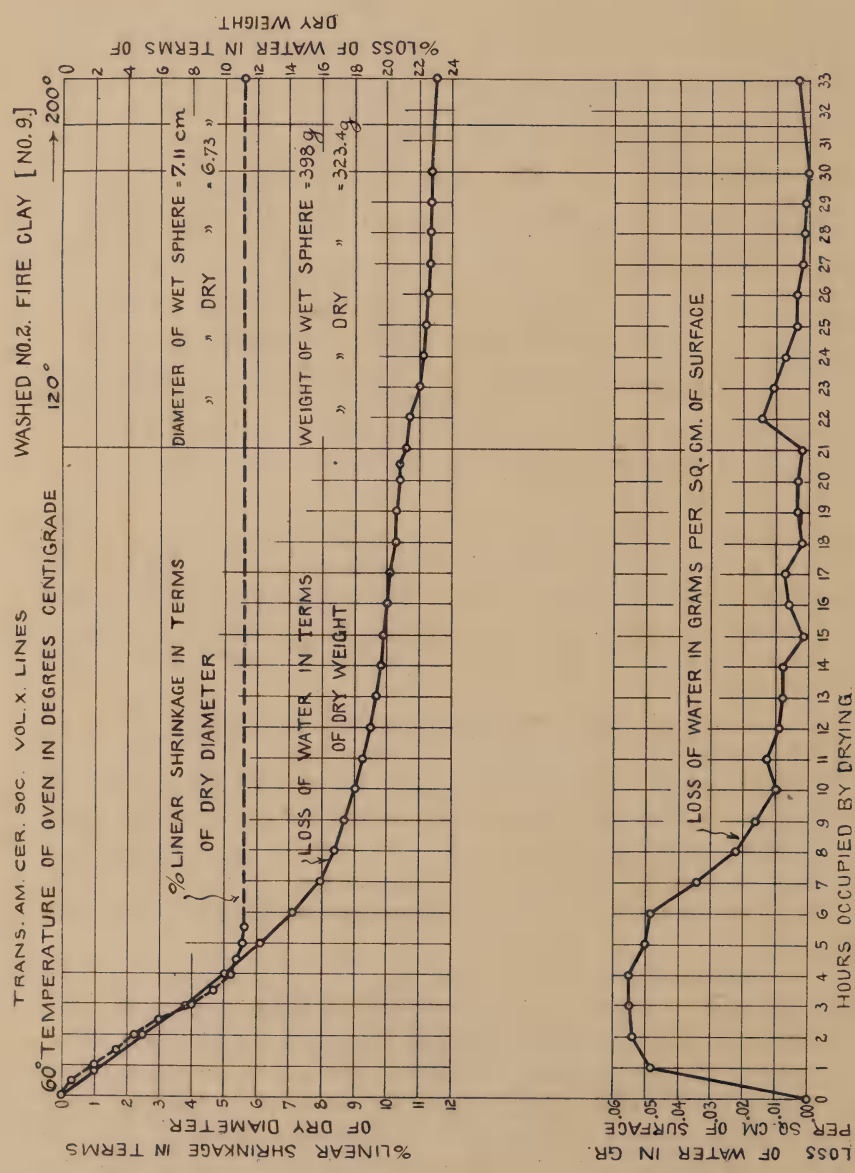
It was originally planned to carry on the whole of the drying at a temperature of 60° Centigrade, as this would produce fairly rapid evaporation without causing a disrupting pressure from steam. This temperature, while it gave very satisfactory results during the early part of the

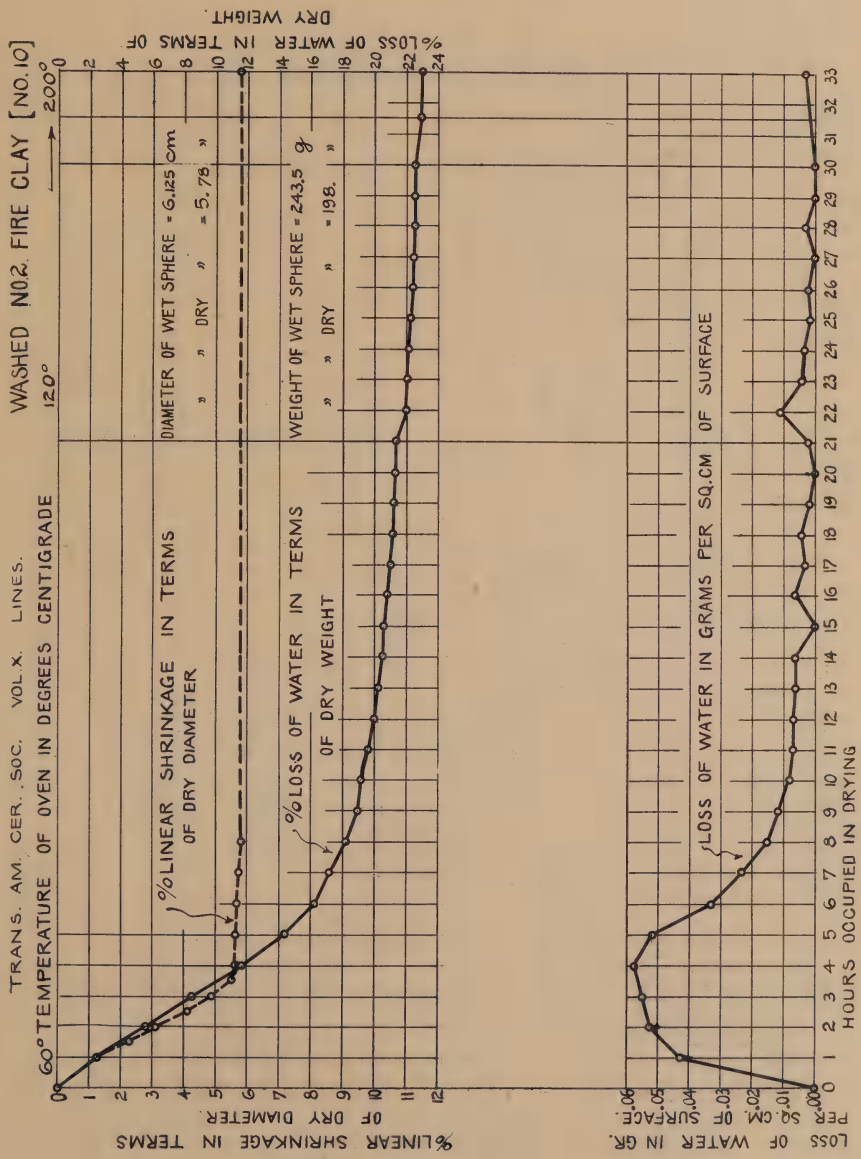
drying, became too slow during the latter part. This plan was abandoned, therefore, and a temperature of 60° was maintained only until weights began to be constant and then it was raised to 120°, where it was held until weights again became constant. At this point a final raise to 200° maintained for one hour was deemed sufficient to remove all pore water. In the whole series only one clay gave trouble in drying. A crack about 2 cm. in length developed in one of the large spheres of washed No. 2 fire clay.

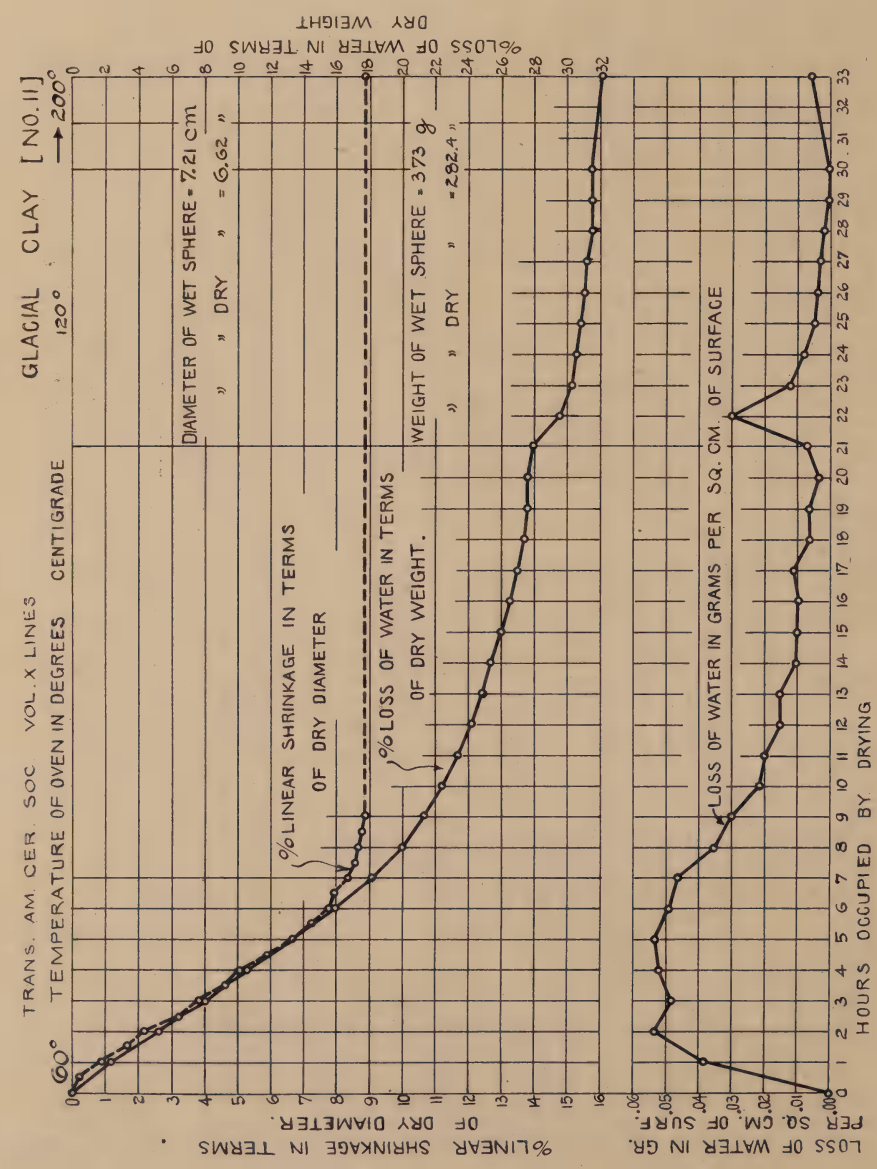
When the drying experiments had been completed, portions of the shale, washed No. 2 fire clay and glacial clay used in spheres 9 to 14, were mechanically separated. The method pursued was as follows: Fifty grams of each material were placed in ½ pint jars of water, to which a little ammonia was added to break up flocculations of fine clay particles, and allowed to slake two days, during which time the clays were occasionally given a vigorous shaking by hand. After boiling one hour the materials were washed through 20, 60, 100, 150, and 200 mesh sieves, after which one further separation was made by removing, by means of a syphon, all clay particles which did not settle in one minute.

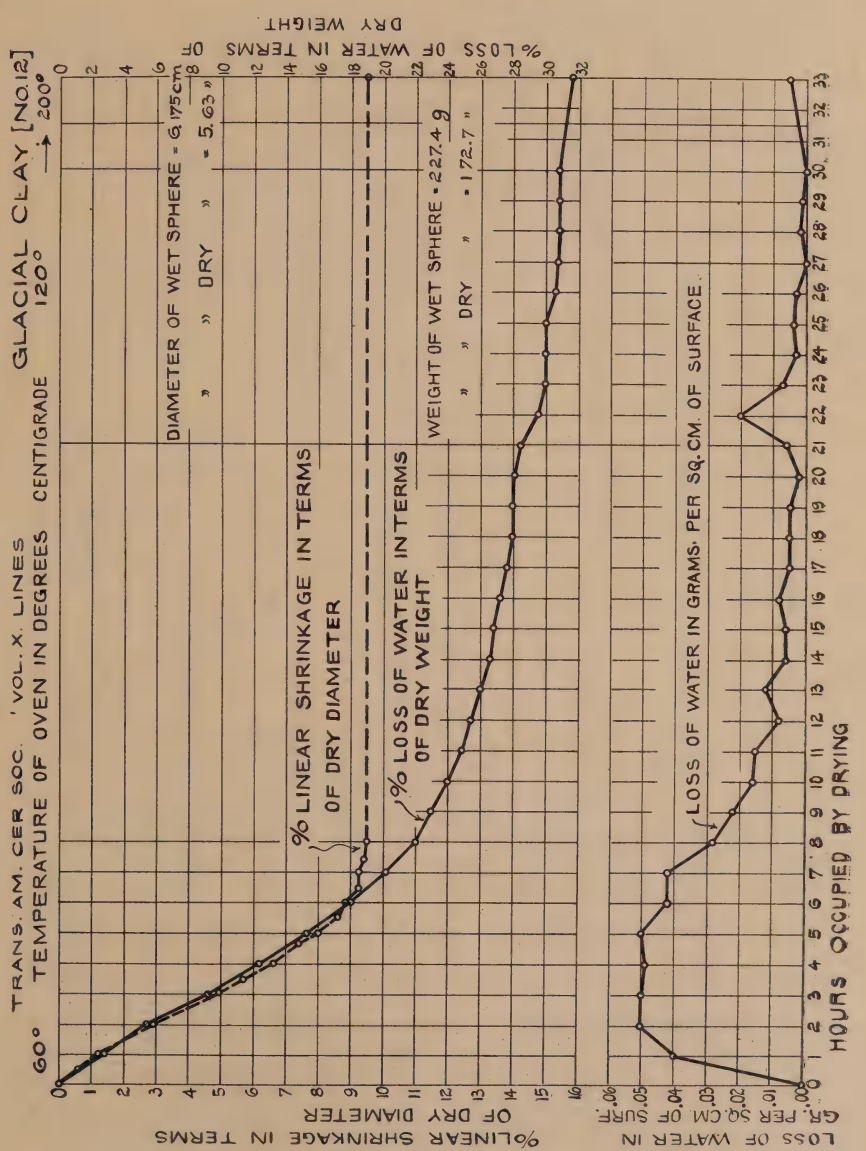
Some of the drying phenomena of spheres Nos. 9 to 14 are shown by means of curves on Plates I to VI. The shrinkage is given by percentage in terms of the dry diameter while the loss of water is shown in two aspects; first, percent loss in terms of the dry weight, and second, by hourly loss in grams per square centimeter of surface. The surface was calculated from the average diameter for each hour.

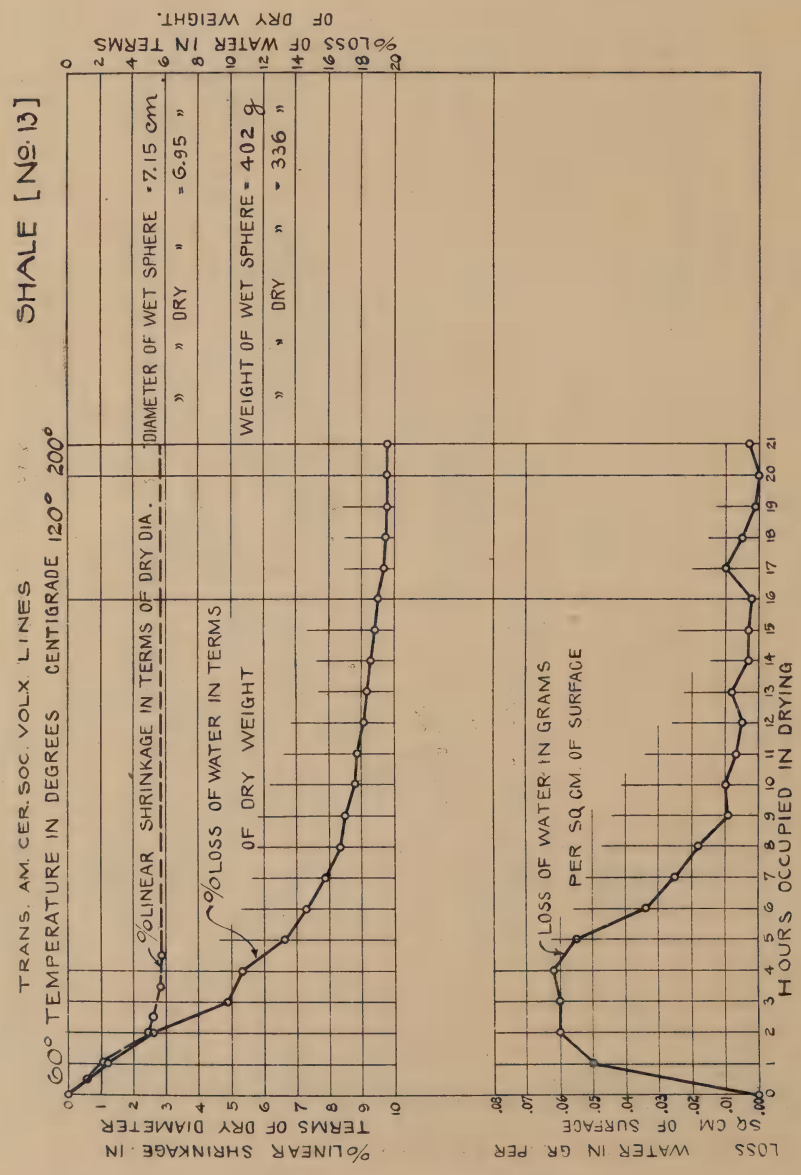
An examination of the curves reveals, as is to be expected, a longer period of shrinkage for the large spheres than the small ones, but it is to be noted that the period of maximum shrinkage is the same for both sizes, viz.: two hours for the shale, 3½ hours for the washed fire clay and 6 hours for the glacial clay. The curve showing percent loss of water affords an opportunity of comparing the relation of shrinkage to evaporation. The variation of

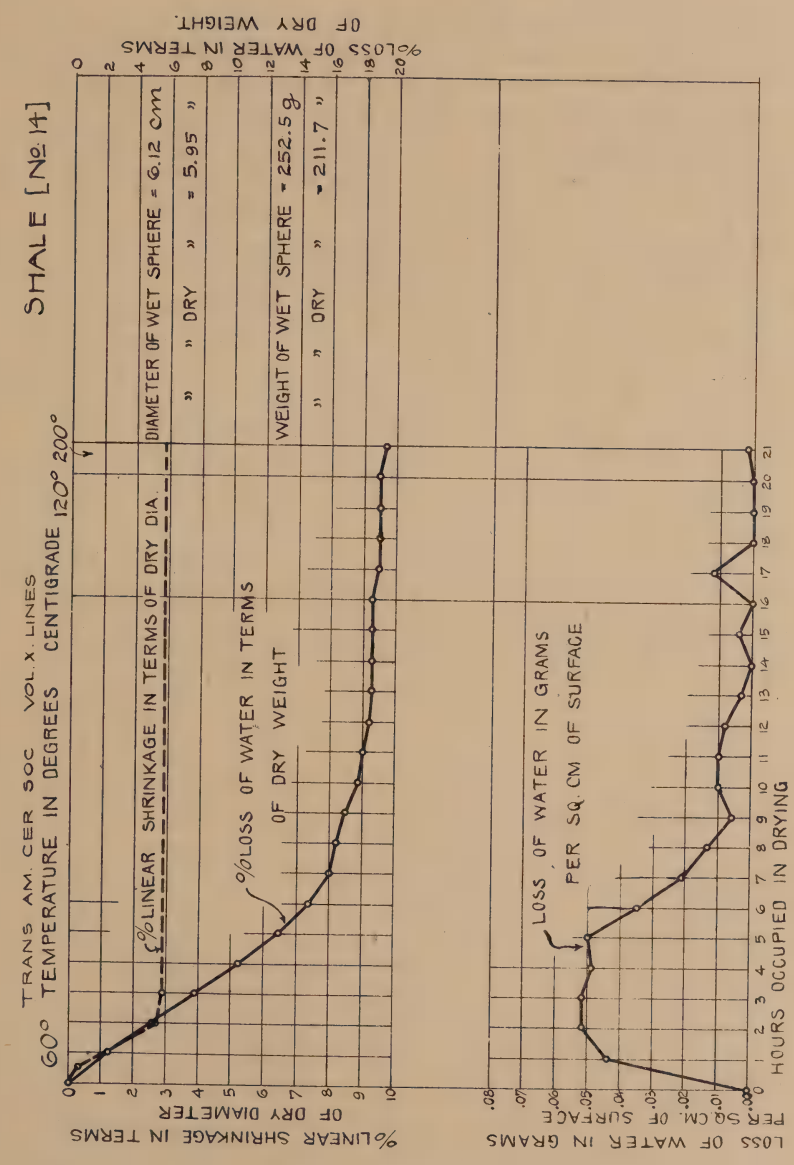

TRANS. AM. CER. SOC. VOL. X LINES
WASHED NO. 2. FIRE CLAY [NO. 9]
60° TEMPERATURE OF OVEN IN DEGREES CENTIGRADE 120° → 200°
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT
DIAMETER OF WET SPHERE = 7.11 cm
" " DRY " = 6.73 "
WEIGHT OF WET SPHERE = 398 g
" " DRY " = 323.4 g
%LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
%LOSS OF WATER IN TERMS OF DRY WEIGHT
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
LOSS OF WATER IN GR. PER SQ. CM. OF SURFACE
HOURS OCCUPIED BY DRYING


TRANS. AM. CER. SOC. VOL. X. LINES.
WASHED NO2. FIRE CLAY [NO. 10]
60° TEMPERATURE OF OVEN IN DEGREES CENTIGRADE
120°
200°
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT
DIAMETER OF WET SPHERE = 6.125 cm
" " DRY " = 5.78 "
WEIGHT OF WET SPHERE = 243.5 g
" " DRY " = 198. "
% LOSS OF WATER IN TERMS OF DRY WEIGHT
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
LOSS OF WATER IN GR. PER SQ. CM. OF SURFACE
HOURS OCCUPIED IN DRYING


TRANS. AM. CER. SOC. VOL. X LINES
GLACIAL CLAY [NO. II]
60° TEMPERATURE OF OVEN IN DEGREES CENTIGRADE 120° → 200°
DIAMETER OF WET SPHERE = 7.21 cm
" " DRY " = 6.62 "
WEIGHT OF WET SPHERE = 373 g
" " DRY " = 282.4 "
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT.
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER.
% LOSS OF WATER IN TERMS OF DRY WEIGHT
LOSS OF WATER IN GR. PER SQ. CM. OF SURF.
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
HOURS OCCUPIED BY DRYING


TRANS. AM. CER SOC. VOL. X. LINES
GLACIAL CLAY [NO. 12]
60° TEMPERATURE OF OVEN IN DEGREES CENTIGRADE 120° → 200°
DIAMETER OF WET SPHERE = 6.175cm
" " DRY " = 5.63 "
WEIGHT OF WET SPHERE = 227.4 g
" " DRY " = 172.7 "
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT
GR. LOSS OF WATER IN GRAMS PER SQ. CM. OF SURF.
HOURS OCCUPIED BY DRYING


SHALE [No. 13]
TRANS. AM. CER. SOC. VOL. X. LINES
60° TEMPERATURE IN DEGREES CENTIGRADE 120° 200°
DIAMETER OF WET SPHERE = 7.15 cm.
" " DRY " = 6.95 "
WEIGHT OF WET SPHERE = 4.02 g
" " DRY " = 3.36 "
% LINEAR SHRINKAGE IN TERMS OF DRY DIA.
% LOSS OF WATER IN TERMS OF DRY WEIGHT
% LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
% LOSS OF WATER IN TERMS OF DRY WEIGHT.
LOSS OF WATER IN GRAMS PER SQ CM. OF SURFACE
LOSS WATER IN GR PER SQ CM OF SURFACE
HOURS OCCUPIED IN DRYING


SHALE [No 14]
TRANS AM. CER SOC VOL. X. LINES
60° TEMPERATURE IN DEGREES CENTIGRADE 120° 200°
DIAMETER OF WET SPHERE = 6.12 cm
" " DRY " = 5.95 "
WEIGHT OF WET SPHERE = 252.5 g
" " DRY " = 211.7 "
%LINEAR SHRINKAGE IN TERMS OF DRY DIA.
%LOSS OF WATER IN TERMS OF DRY WEIGHT
%LINEAR SHRINKAGE IN TERMS OF DRY DIAMETER
%LOSS OF WATER IN TERMS OF DRY WEIGHT
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
LOSS OF WATER IN GRAMS PER SQ. CM. OF SURFACE
HOURS OCCUPIED IN DRYING

the latter is greatly emphasized by the curve illustrating the loss of water in grams per square centimeter of surface. It may be noted, however, that in spheres 9 and 10 the average rate of loss during the first five hours, a period of maximum evaporation, is .052 grams each, and for spheres 11 and 12 it is .049 and 0.048 grams. This consistency is lacking in spheres 13 and 14 where the average rates for the same period are .057 and .049 grams.

Some of the earlier experiments seemed to indicate that there was a relationship between shrinkage and rate of loss of water, but the later ones do not bear it out. The period of maximum evaporation seems to be largely independent both of shrinkage and size of sphere. While there is considerable difference in the total shrinkage, time required for same and total loss of water in spheres 10, 13 and 14, the period of maximum evaporation is five hours in each case.

Another lack of connection is between the shrinkage and amount of pore water. While the percent shrinkage of shale, fire clay and glacial clay is roughly in the ratio 3 : 6 : 9, the percentages of pore water are 11, 10 and 12.

Some of the data from the whole series of drying experiments are given for comparison in the table below:

TABLE OF DRYING DATA.

Number of Sphere	Hours required to complete shrinkage at 60° C.	*Percent. of Linear Shrinkage.	†Total Percent. of Water Lost in Drying at 60-200° C.	†Percent. of Water Remaining at End of Shrinkage.	†Percent. of Water Lost at 120° C.	†Percent. of Water Lost at 200° C.
1	4	4.0	23.5	13.3	a	a
2	3½	3.4	22.9	11.2	a	a
3	3½	4.0	22.7	14.5	a	a
4	3	3.2	21.6	13.0	a	a
5	4½	4.5	20.3	11.0	a	a
6	3	4.5	19.8	11.9	a	a
7	6½	5.1	20.7	8.7	a	a
8	4	5.0	20.6	10.9	a	a
9	5½	5.6	23.1	9.9	1.8	0.5
10	3½	5.8	23.0	10.1	1.2	0.5
11	8½	8.9	32.1	11.2	3.5	0.6
12	6½	9.5	31.7	12.7	2.2	1.0
13	3½	2.9	19.6	10.4	0.4	0.2
14	3	2.9	19.3	11.6	0.6	0.2

Nos. 1, 2 Shale from Galesburg, Illinois.

Nos. 3, 4, 13, 14 Shale from Streator, Illinois.

Nos. 5, 6, 9, 10 washed No. 2 fire clay from Colchester, Illinois.

Nos. 7, 8 unwashed No. 2 fire clay from Monmouth, Illinois.

Nos. 11, 12 Glacial clay from Urbana, Illinois.

Odd numbers refer to large spheres and even numbers to small ones.

*In terms of dry diameter of sphere.

†In terms of dry weight of clay.

[a]Not dried at 120° and 200°.

On averaging the percentages of loss of water and expressing them in terms of the dry weight of the clay, we obtain the following figures:

AVERAGES OF DRYING DATA.

CLAY	Total per cent of loss of Water	Per cent of Shrinkage Water	Per cent of Pore Water	Per cent of Water Lost after reaching constant weight at 60°
Streator Shale	20.8	8.4	12.4	0.7
Galesburg Shale	23.2	10.9	12.3	0.6
Washed No. 2 Fire Clay	21.5	10.8	10.7	2.0
Unwashed No. 2 Fire Clay	20.6	10.8	9.8	2.6
Glacial Clay	32.4	20.4	12.0	3.2

In the above table the clays are placed in the order of rapidity in drying, the Streator shale being the most rapid and the glacial clay the slowest. While the figures indicate consistent relations between amount of water and time of drying in the extreme types, they fail to show the same relationship for the clays having more nearly the same water content.

A further relation between the different types of clays is brought out in the following table of sizes of grain:

TABLE SHOWING RESULTS OF MECHANICAL SEPARATION.

MATERIAL	Residue Left on Screens					Residue 1 minute Settling	Remainder by Difference
	20-Mesh	60-Mesh	100-Mesh	150-Mesh	200-Mesh		
Shale (Streator)	1.8	5.2	3.5	4.6	3.0	16.8	65.1
Washed Fire Clay	0.0	0.7	1.4	2.1	1.5	12.3	82.0
Glacial Clay	0.6	7.3	4.4	2.9	0.9	16.1	67.8

In comparing this table with the table of averages given above it will be noted that the relation between size of grain and per cent of pore water is not established until the 200 mesh screen is reached. The amount of material

passing the 200 mesh screen is greatest where the percentage of pore water is lowest and least where the percentage of pore water is highest. The subtraction of the residue by one minute settling does not alter this relationship.

The facts set forth in the curves and tables accompanying this paper are suggestive rather than convincing. The data are not numerous enough to justify empirical statements, but are placed on record to be of such service for comparison as opportunity offers.

DISCUSSION.

Mr. Parmelee: I think the form of the trial piece is worthy of note, since the sphere is a much more rational shape than any other. It seems to me the sphere would be the most useful shape to use in the determination of specific gravity of clays. I will ask the chair whether he ever compared the sphere with any other shape in regard to that condition?

The Chair: I have made no such comparisons.

Mr. Parmelee: In weighing a soaked piece, the surface exposed would be far less in a sphere than any other shape. I was curious to know whether you had compared two shapes and found any difference as to exposure to the atmosphere.

THE FUNCTION OF BORON IN THE GLAZE FORMULA.

BY

CHARLES F. BINNS.

Some eight years ago the writer conducted an investigation upon the constitution of raw lead glazes and showed that the most satisfactory relationship of base to acid was as one to two on the oxygen ratio, the resulting glazes being molecular monosilicates. Following upon this a general agreement was arrived at by which the acidity of all glazes was computed as to the oxygen content, so that the glazes referred to became known as bisilicates. At the close of the paper upon this subject the following remark was made: "So far as we have gone the monosilicate ratio cannot be departed from in raw lead glazes * * * it is certain that the introduction of boric acid will demand a new set of conditions."

These words were criticised at the time with the statement that if boric glazes did not conform to the rule expressed, it would throw considerable doubt upon the accuracy of ceramic science. This criticism is reasonable because there is nothing to show that the laws of chemical combination are violated, whatever substances are brought into union with each other.

Not very much work has hitherto been done upon the function of boron itself. Seger considers it acidic in behavior, and says that it behaves in a manner similar to silica, except as to the point of fusion.

Messrs. Purdy and Fox, in the paper upon fritted glazes published last year, contradict this, stating that the function of boric compounds is rather to counteract devitrification, and that the coefficient of expansion of a glaze is increased rather than diminished by their use.

Several ceramists when working upon fritted glazes have been struck by the fact that so far from boric acid

replacing silica, the introduction of this ingredient has necessitated an increase of the silica content. For instance, a normal raw glaze may correspond to the formula

$$RO,\ .2\ Al_2O_3,\ 1.6\ SiO_2$$

If now, .3 B_2O_3 be added to the acid content, it is found in practice that the silica must be increased to 2.5, producing the following as a normal fritted glaze:

$$RO,\ .2\ Al_2O_3,\ 2.5\ SiO_2$$
$$0.3\ B_2O_3$$

It will at once be seen that the oxygen ratio of this glaze is no longer 1 : 2 but has risen to 1 : 3.7. No one has attempted to explain this discrepancy, but about eighteen months ago Mr. Paul E. Cox, a graduate of the New York School of Ceramics exclaimed to the writer, "Boron is basic!" Great is the value of imagination! The professor had, for the want of a touch of this saving grace, been floundering in a morass of doubt. The student came to the rescue and with a word established what appears to be a solid foundation.

The first thought was that B_2O_3 should be considered as BO, and placed in the RO column with an equivalent weight of 62. After a few trials this was found to be impracticable, because of the difficulty of making room in the formula for the necessary amount of the ingredient. Besides this it involved the hypothesis of a borous compound for which chemistry at present affords no warrant.

A search through the chemical and mineralogical authorities gave but little information. The mineral datolite is defined by Dana as a silicate of boron and calcium, and mention of the sulphide and chloride of boron is made in the chemistry books.

It was noticed that from its position in the periodic curve and from its valence, boron might be presumed to act like aluminum, functioning as a base with strong acids and as an acid with strong bases. This would place B_2O_3 in the R_2O_3 column as boron sesquioxide, which indeed is

the accurate chemical definition of the anhydrous substance. Now if the formula given above be examined in the light of this statement it will be found that the glaze falls into line as a bisilicate.

$$\begin{matrix} RO, & Al_2O_3\ .2 & SiO_2\ 2.5 & \text{Oxygen ratio } 1:2 \\ & B_2O_3\ .3 & & \end{matrix}$$

So far the presumption was in favor of this solution, and some definite synthetical work could be undertaken.

The first question was as to whether boron sesquioxide could be directly combined with silica. A mixture was made up with precipitated silica in order to facilitate the reaction. The formula was $B_2Si_2O_7$. Fusion of the mix at cone 6 resulted in a milk white glass. This was pulverized and submitted to the prolonged action of hot distilled water. The powder was almost completely hydrolized. Flocculent silica separated, and the clear filtrate was found to contain a considerable amount of silica in solution. The evidence was that boron sesquioixde could completely dissolve precipitated silica, but there was no indisputable evidence of combination.

A similar mix was made up with ground quartz and fused at cone 6. The pulverized fritt was more easily attacked by water than that made with precipitated silica. but after long heating a large residue of powdered glass was found which resisted all aqueous action. This was not undissolved quartz but a clear amorphous glass. It was then determined to attack the problem by means of the phenomenon of combination heat.

A small gas muffle was fitted with a clay-ware door which was entered by a long open tube. The tube was large enough to permit the introduction of a platinum crucible by means of a long pair of tongs. A Fery radiation pyrometer was focused upon the opening, and the furnace was brought to constant temperature at about 1200°C. When this constant had been secured an empty platinum crucible was quickly introduced and it was found that a sudden chill was indicated, the heat rapidly rising again but not to the

previous constant point. The explanation of this is that the heat of combustion and the loss by radiation were at an even balance so that the absorption of a small amount of heat by the crucible gave a permanent fall of temperature. The pyrometer curve then took the form shown in Fig. I.

A second crucible was now filled with the boron silicate mixture and introduced as before. The same chill was shown by the pyrometer, but now as the crucible gathered heat and the charge began to melt, the curve rose above the previous constant and then fell to a second and lower level, as shown in Fig. II.

This experiment was repeated several times at temperatures ranging from 1100° to 1200°, but the result was the same, with slight variations, in each case.

The evolution of heat was undoubted, but the suggestion was made that this might be a heat of solution and not of combination. It was, therefore, determined to try other mixtures. Two suggestions presented themselves. $Ca_2B_4O_8$ would illustrate the acid function of boron, and $Na_2Si_2O_5$ would present an analogy as to the evidence of combination with silica. Both these mixtures gave the characteristic curve of heat of combination. Boric sesquioxide alone showed no heat evolution whatever, nor did the boron silicate glass pulverized and remelted. The heat evolved may have been a heat of solution, but if so the heat evolved from the soda-silica melt is analogous.

It matters little what name is given to the reaction because chemistry cannot yet show whether glazes are to be classed as solutions or as combinations.

The evidence cited up to this point is in favor of a direct reaction between silica and boron sesquioxide, and no one to whom these experiments have been submitted has had the hardihood to suggest that silica is the base.

This portion of the work is presented with some diffidence. The writer makes no claim to be an experimenter of the experience demanded by such delicate operations as those detailed, but every opportunity has been seized

Fig. I.

CURVE OF EMPTY CRUCIBLE.

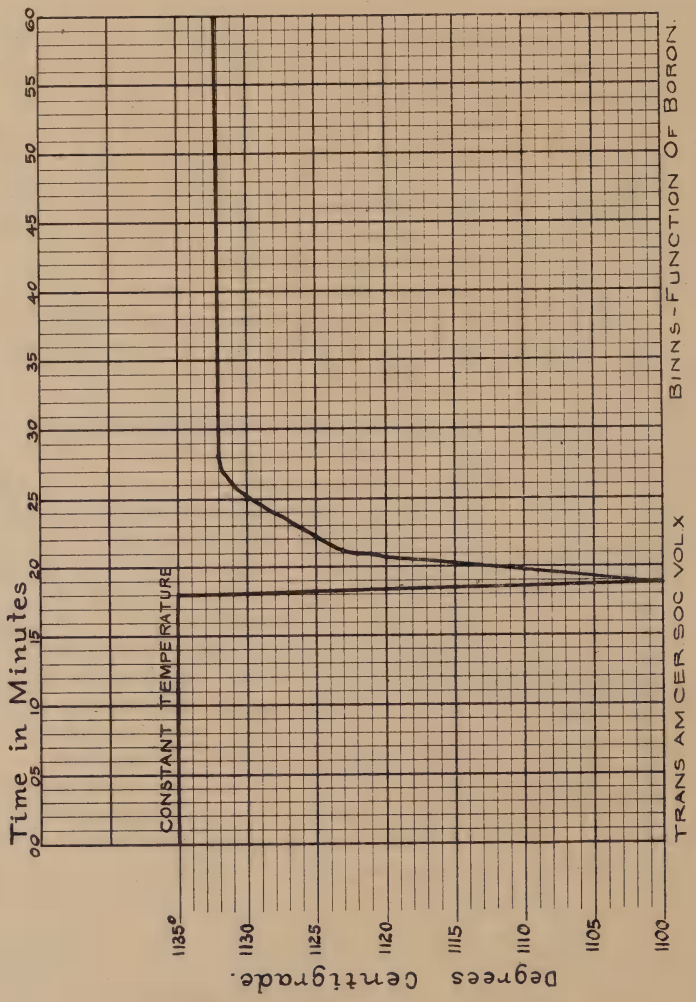
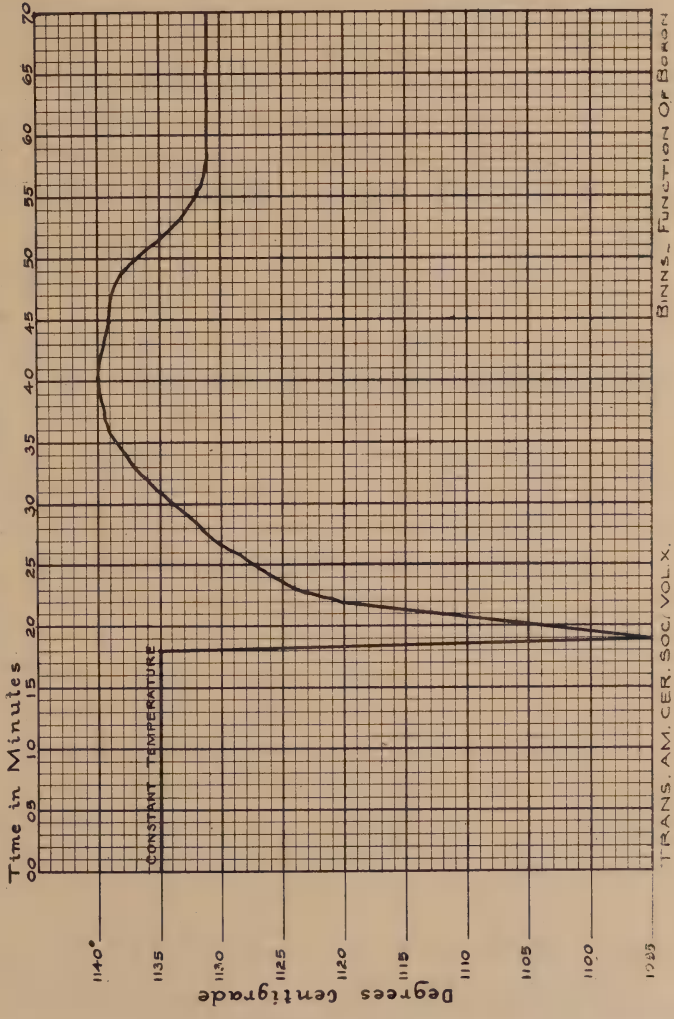


Fig II.

TYPICAL CURVE OF CRUCIBLE CHARGED WITH MIXTURE $B_2Si_2O_7$


Time in Minutes
00 05 10 15 20 25 30 35 40 45 50 55 60 65 70
CONSTANT TEMPERATURE
Degrees Centigrade
1140° 1135 1130 1125 1120 1115 1110 1105 1100 1095
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of consulting men of expert knowledge in chemistry and physics, and, so far, all have agreed in the conclusions.

The second question to be answered was whether B_2O_3 could be shown to function as a base in the composition of glazes. In this the writer is on more familiar ground, and as a net result, the opinion is expressed that B_2O_3 undoubtedly is basic when melted with silica or silicates, and that it may be used to replace alumina partially or entirely, with the exception of its exercise of the property of fusibility.

This conclusion has been reached with some searchings of heart, for it has involved the reversal of some previous teaching and a retreat from a position previously held.

Some of the experiments will be detailed here, and specimens of the results are shown.

SERIES XIV.

No. 1.

$$\left.\begin{matrix}.40\ PbO \\ .25\ CaO \\ .20\ ZnO \\ .15\ KNaO\end{matrix}\right\} \left\{\begin{matrix}.20\ Al_2O_3 \\ .05\ B_2O_3\end{matrix}\right\} 1.75\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 2.
O. R. with Boron as Acid 1 : 2.2.
Ratio of R_2O_3 : SiO_2 1 : 7.

No. 6.

$$\left.\begin{matrix}.20\ ZnO \\ .40\ CaO \\ .25\ PbO \\ .15\ KNaO\end{matrix}\right\} \left\{\begin{matrix}.05\ Al_2O_3 \\ .20\ B_2O_3\end{matrix}\right\} 1.75\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 2.
O. R. with Boron as Acid 1 : 3.39.
Ratio of R_2O_3 : SiO_2 1 : 7.

The arrangement of lead oxide and calcium oxide in the RO content was made so as to adjust the fusibility of the glazes. Otherwise that containing the larger amount of B_2O_3 would have melted too easily. These two glazes with four intermediate members show remarkable uniformity. If B_2O_3 had functioned as an acid, making glaze

No. 1 little more than a bisilicate and No. 6 higher than a trisilicate, it is scarcely credible that the uniformity would have been secured; however, the varying content of lead oxide and calcium oxide may have had something to do with the result.

Following upon this the alumina was omitted entirely and boron was relied upon as a flux with the assistance of barium.

SERIES XV.

No. 1.

$$\left.\begin{matrix} .300\ CaO \\ .250\ BaO \\ .200\ ZiO \\ .125\ K_2O \\ .125\ Na_2O \end{matrix}\right\} \left\{ .25\ B_2O_3 \right\} 1.75\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 2.
O. R. with Boron as Acid 1 : 4.
Ratio of R_2O_3 : SiO_2 1 : 7.

No. 6.

RO as in No. 1 .50 B_2O_3 2.5 SiO_2

O. R. with Boron as R_2O_3 1 : 2.
O. R. with Boron as Acid 1 : 6.
Ratio of R_2O_3 : SiO_2 1 : 4.6.

Four intermediates were made up and the series burned at cone 2. Naturally the glazes are less fluid than those of Series XIV, but it happens to be the case that XV 1 with .25 B_2O_3 is more fluid than XV 6 with .5 B_2O_3. This series demonstrates that B_2O_3 may be used to replace Al_2O_3 entirely, at least in an experimental way, and further indicates that B_2O_3 in excess tends to act as Al_2O_3 in increasing the viscosity of a glaze. This point is also illustrated in the next series to be considered.

SERIES V.

No. 1.

$$\left.\begin{matrix}.234\ ZnO \\ .297\ K_2O \\ .469\ CaO\end{matrix}\right\} \left.\begin{matrix}.234\ Al_2O_3 \\ .290\ B_2O_3\end{matrix}\right\} 2.358\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 1.8.
O. R. with Boron as Acid 1 : 3.1.
Ratio of R_2O_3 to SiO_2 1 : 4.5.

No. 11.

$$\left.\begin{matrix}.234\ ZnO \\ .297\ K_2O \\ .469\ CaO\end{matrix}\right\} \left.\begin{matrix}.234\ Al_2O_3 \\ .290\ B_2O_3\end{matrix}\right\} 3.4\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 2.6.
O. R. with Boron as Acid 1 : 4.
Ratio of R_2O_3 to SiO_2 1 : 6.4.

All these glazes present the appearance which is usually attributed to an excess of alumina. They are full of minute bubbles which indicate extreme viscosity, and have consequently a leathery surface. The content of alumina alone is not unreasonable, being .234 equivalent, but when the content of B_2O_3 is added, the total R_2O_3 becomes .524, which is very high. The oxygen ratio ranging from 1 : 1.8 to 1 : 2.6 includes the bisilicate.

Series XVIII is interesting as showing a development of devitrification. The formula is:

No. 13.

$$\left.\begin{matrix}.35\ BaO \\ .10\ CaO \\ .21\ K_2O \\ .14\ Na_2O \\ .20\ ZnO\end{matrix}\right\} .28\ B_2O_3 \left.\right\} 1.84\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 2.
O. R. with Boron as Acid 1 : 4.
Ratio of R_2O_3 to SiO_2 1 : 6.5.

No. 18.

$$\left.\begin{matrix} .35\ BaO \\ .10\ CaO \\ .21\ K_2O \\ .14\ Na_2O \\ .20\ ZnO \end{matrix}\right\} \parallel .28\ B_2O_3 \Big\} 2.76\ SiO_2$$

O. R. with Boron as R_2O_3 1 : 3.
O. R. with Boron as Acid 1 : 6.
Ratio of R_2O_3 to SiO_2 1 : 9.8.

It seems incredible that if B_2O_3 here functions as an acid there should not have been devitrification in all glazes, but if No. 13 be a bisilicate and No. 18 a trisilicate, the phenomenon is just what would be expected.

It should, perhaps, be explained that in this study no attempt was made to prepare good glazes. Rather the contrary, for the faults of glaze are more eloquent than their excellences. Perhaps the work may be continued before publication to the extent of developing some perfect glazes by the use of the principle suggested. A good deal of time has been spent in standardizing and adjusting conditions, the results of which would only be tedious in recital.

The reasons advanced for the assignment of boron sesquioxide to the R_2O_3 column may be summed up under the following heads:

1. Analogy. So far as we are aware all of the sesquioxides exert both acid and basic functions. There are ferrates and salts of iron, chromates and salts of chromium, antimoniates and salts of antimony, aluminates and salts of aluminum. Then why not borates and salts of boron? Silicon dioxide exerts, under fire, the most powerful acidic function known, and there is every reason to believe that boron silicates would be formed in fusion.

2. Reaction. It has been shown that upon the melting of silica and boron sesquioxide together, heat is evolved which can be measured over and above the heat of the furnace. If this be a heat of solution then a similar reaction takes place between silica and sodium oxide.

3. Practice. Glazes containing boron sesquioxide do not obey the bisilicate law if boron be regarded as acidic, but this law is immediately obeyed if the boron be regarded as basic.

DISCUSSION.

Dr. Zimmer: The character of Mr. Binns' paper is such that it is really very hard to discuss it. While I admit that all the facts brought out seem to indicate that boron will act as a base, there are surely conditions under which it will act as an acid.

While not doubting any of those facts, I want to call the attention of the Society to a few experiments made by myself with regard to the melting of silicic acid with boracic acid at comparatively low temperatures. I am satisfied that the flux obtained was nothing but a solution, as I was able to dissolve in hot water all the boracic acid. At the same time I found some fluxes or glasses where I had to add muriatic acid to help to recover the boracic acid. There is another fact which indicates that boron in the glaze acts as an acid; if in firing, you use a coal which contains a high percentage of sulphur, you will find that a glaze high in boron may occasionally show signs of devitrification, which must, to a certain extent at least, be attributed to the expulsion of boracic acid. I believe in a paper which Mr. Hottinger read at our third annual meeting he brought out the fact that the boracic acid of the odd numbers of the Seger cones is to a great extent expelled by sulphuric acid. The boracic acid enters those mixtures as an acid and not as a base.

To come back to where I started, I beg to say, that this paper is a very interesting one. It opens up quite a new field. It brings before us new ideas to be followed up and studied. If, however, boron really acts as a base, under certain conditions, there are surely others under which it will act as an acid.

Mr. Langenbeck: I thank you, gentlemen, and I thank the President for giving me an opportunity to dis-

cuss this subject. The ideas advanced in this paper are so new and so full of meat, that it would take considerable hardihood to advance any positive opinions in the face of such experiments, and I am not prepared to do so, though undoubtedly the fact that a more acid boron-silicate glaze is required, to stand on the same body, than a silica glaze, must have given all of us more or less qualms. While I must confess I never made the experiments which Mr. Binns here suggests, I am extremely interested and my prejudices are rather in his favor, if my convictions are not yet prepared to follow.

I will ask Mr. Binns, as in our green days of chemical superiority over practice we laughed much at the Trenton flux of boracic acid and silica,—whether he or anyone else present ever went to the trouble to see whether *all* the boracic acid disappeared in the grinding of the glaze and was carried out of solution by the glaze water afterwards siphoned off; or whether he did as most of us did, took it for granted and never submitted it to investigation? It seems to me Mr. Binns must have thought of that flux when he was making these experiments, and I would like to have his reflections on this subject.

Mr. Mayer: Mr. President and Gentlemen: I am not prepared to discuss the paper. All the theories I have had in the past concerning the action of boracic acid are certainly knocked in the head if Professor Binns' conclusions are correct.

If I understand Professor Binns correctly, he stated that we can replace alumina by boracic acid. Now, if that is correct, it interests me. I have lately been trying to solve the problem of what is called in England some "tender" colors. The only way to get these colors is to cut the boracic acid out. If this idea is correct, that you can replace alumina by boracic acid—I don't think you claim that it would not affect the solvent action?

Mr. Binns: No, sir.

Mr. Mayer: Then I am talking off the book, as Professor Binns does not claim it does not affect the solvent action.

Regarding the point raised by Mr. Langenbeck about the fritting of boracic acid and flint together, I am positive that a large percent of boracic acid goes into solution after fritting at cone five or six, from experiments I have made, but I cannot say it all goes out. I do not know that I care to discuss the paper at the present time, as it brings up a new matter entirely; and I think we will have to study it and do a little experimenting along our own lines before we can talk intelligently.

Mr. Burt: I have not myself made any particular study of the boracic acid or boron question, except as to the one fact stated in a paper some time ago, that I was unable to account for its coefficient by any of Seger's rules. I said that it seemed, as far as I could see, directly opposed to the rules which Professor Seger gave us, which was further proved by other papers. I do not know but this paper may possibly throw light on the subject. In the question of replacing Al_2O_3 by B_2O_3, it is not clear whether Professor Binns thinks he would arrive in that substitution at an equivalent coefficient, that is, whether he would give B_2O_3 the same equivalent as Al_2O_3, and thus have the same results with either in crazing or non-crazing.

Mr. Stover: As Mr. Langenbeck referred to the work of the Trenton potters, I will say a word. I don't want to stand as the representative of the practical potter in Trenton, for I think he needs no apology—we have one with us, our Vice-President. They have continued to frit boracic acid and flint, notwithstanding what the American Ceramic Society has said to the contrary. In my efforts to prove that the scientific side was the one they should come over to, I have taken the water from the top of the glaze pan, evaporated it off, and showed them their boracic acid in solution. I was able to prove that. I made some experiments along the line, but I haven't the figures. I got the answer, "We have been doing it for years and it has worked well enough and we will continue to do it." They say, "You are only guessing—we don't throw that water away."

Mr. Purdy: When glazing red bodies our seniors

noted an opalesence in the glaze to which they had added boracic acid. That opalesence appeared with the addition of boracic acid. Of course, we only have the coincidence of the appearance of opalesence with the addition of boracic acid; but the very fact that it was this substance (unknown) in suspension in the glaze, which I showed last year would crystallize under proper heat treatment, is evidence that it possibly is a boron silicate. I have not analyzed the situation carefully. I know there are boron phosphates, and I know that all attempts to show that boron is a base have, as a rule, failed; and that the boron phosphates, boron chlorides, etc., are rather unstable compounds. In environments to be found in a fused glaze, boron might possibly be combined with an acid, for instance, forming a boron silicate.

Mr. Plusch: I will ask Professor Binns if the boron was fritted before it was added to the glaze? Second, if you fritted it, in the place of alumina, what medium you used to apply the glaze? Next, whether you applied it to the green or to the biscuit tile; and if to the biscuit, what amount of porosity was there in the tile?

Mr. Parmelee: In a discussion with Mr. Bowman, it occurred to me that there are borate glasses which are very useful on account of their optical properties. It is quite contrary to our conception of glasses to have any agent present which would be likely to cause devitrification. How can we reconcile those two different functions? It seems to me impossible to say, except with respect to the alkali group, that any single element possesses only basic or only acidic properties. Other conditions which prevail will determine the action of the element. At low temperatures we have compounds in which boron is combined with more strongly acid elements or radicals, and it seems to me difficult to determine whether it is acid or basic. It is a very interesting question to consider.

The Chair: I could not discuss this paper adequately, for the subject is a deep one. If Professor Binns' conception is right, we will have to overthrow many of our notions

of boracic acid. It seems to me it requires further work, and we must attack the problem by other methods before we can arrive at a final conclusion, and follow Ostwald's advice to attack a problem by as many methods as possible.

Mr. Binns: Mr. President and Gentlemen: I will take up these questions and reply to them seriatim. Dr. Zimmer thought sulphuric acid replaces boron. I think that phenomenon of devitrification may be as well accounted for if the sulphuric acid withdraws the boron from the combination, and the devitrification in that case is more an evidence of basic than acidic function. I admitted right through that boron will function as acid under some conditions but not, I think, in the presence of silica.

Mr. Langenbeck asked if all the B_2O_3 is dissolved when the common frit of boric acid and flint is made. The object of fritting is to render the soluble substances insoluble. If one does not produce an insoluble compound he does not accomplish the purpose of his frit. He may be right as to the process of fritting silica and boric acid, but he may be wrong as to the making of an insoluble frit. There are cases, as my paper states, where a boro-silicate melt is insoluble, or nearly so.

Answering Mr. Mayer's question as to colors, I have not taken that into consideration at all.

Mr. Burt asked as to the replacing of alumina and the effect of the substitution on the coefficient. I found that boric acid has no apparent effect on the coefficient. Messrs. Purdy and Fox stated certain facts as to the effect of the alumina on the coefficient which are yet to be confirmed; but that is not within the point of discussion. I think that boron sesquioxide functions the same way. Boric acid does not cause crazing if it replaces alumina in the proper proportion. I have replaced boric acid by alumina and vice versa without influence on the point of crazing.

Professor Purdy raises the question of opalesence. No person could experiment long on boric glazes without striking that, but I am not yet prepared to discuss the point.

Mr. Plusch asked certain questions. To the first, I

will answer yes, certainly. The boric acid was fritted in the ordinary way. To the second question, as to media used, I used zinc oxide and whiting, and found no difficulty in floating the glaze. In experimental work one must disregard mechanical difficulties. It does not necessarily mean that you can duplicate certain facts in the factory. My purpose was not to make good glazes, and if I had had to use mucilage, or what not, to make the glazes flotative, I would have been justified.

I had two series of bodies, one made up as a non-crazing body, and the other as a crazing body. The non-crazing tile which I used was burned to about cone eight, and burned to a reasonable earthenware hardness. I did not consider it vital to determine the porosity of the tile, it was just about earthenware hardness.

Professor Parmelee alluded the the case of boric glasses, but I did not quite understand his question.

Mr. Parmelee: The point is this: We have a type of glass, boric glass, which is transparent and used for optical purposes. You stated that boric acid would act similar to alumina, and could replace it; if that be so would not devitrification and loss of transparency necessarily follow?

Mr. Binns: Alumina is used to prevent devitrification and so is boric acid. The reason alumina is not used in glasses is on account of its great viscosity.

I want to say one or two things in closing this discussion. I thank you for the consideration you have given this paper. As I explained in my paper, it has caused me a great many searchings of heart, as I shall have to reverse my former teachings if the case be proved. I have always been able to construct bright and matt glazes on paper, at any temperature, and had no doubt as to their serving my purposes; but I have never been able to do this with reference to fritted glazes. They obeyed no law. But now, if my argument be sound, the same law will be obeyed by glazes of every type which is, in itself, strong evidence of truth.

Mr. Parmelee (Note): By devitrification is meant

literally, a loss of the characteristic glass-like properties, chief among which are the amorphous structure and transparency. A good illustration of devitrification is a true matt, that is, a glaze having a cryptocrystalline structure. Such a devitrification may be brought about by a proper adjustment of the alumina-silica ratio. If boric acid possesses in glazes properties similar to those of alumina, it seems reasonable to expect the boric acid to be able to produce devitrification under suitable conditions, just as alumina will do. It would appear from the inspection of analyses given by Horrstadt in "Jena Glass," page 146 (translated by J. D. & A. Everett) that boric acid may be used throughout a wide range without apparently giving rise to devitrification. Final judgment should fairly be withheld until we have the results of more extended research. It is true that alumina is used to prevent devitrification; yet it is also used to induce the phenomenon.

NOTES ON THE USE OF CRUDE OIL FOR BURNING KILNS.

BY

CARL H. GRIFFIN, Worcester, Mass.

In an endeavor to reduce the cost of burning and to obtain a more uniform product by better kiln control, the Norton Company, several years ago, undertook a series of experiments with crude oil as a fuel. While these experiments did not result in the installation of the fuel oil system, they were not entirely unsuccessful, and may prove of interest as a departure from the more accepted methods of firing.

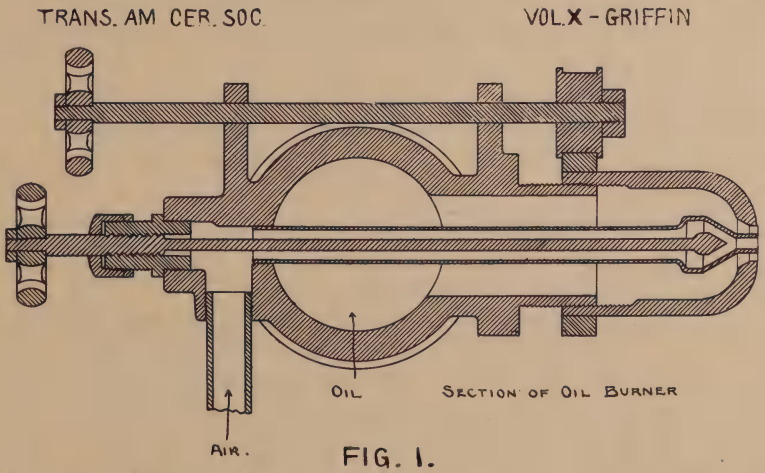

FIG. 1.

The oil used for these experiments was purchased from the Standard Oil Company, under the name of "crude oil." It is composed of the heavier hydrocarbons remaining after the distillation of the benzine, naptha, etc., has a specific gravity of 0.837 and contains only 0.15% of sulphur. The Standard Oil Company's quotation at the time of these experiments was 3½c per gallon in tank car lots.

The apparatus required was loaned the Norton Company by Messrs. Gilbert & Barker, of Springfield, Mass., engineers and contractors for fuel gas and fuel oil plants. It consisted of a number of oil burners, a 500 gallon storage tank, a pump for raising oil to the burners and a Root blower for spraying it into the firebox. Fig. 1 shows a section of one of the burners used.

The first installation of this system was made under Messrs. Gilbert & Barker's supervision, Fig. 2 showing their method of applying to our kiln.

By this arrangement, the oil is forced against a projection (A) from the upper side of the firing door, which serves to break up the stream and cause more rapid and more complete combustion. The kiln was burned three times under these conditions, but with hardly the desired results as regards heat distribution. Most of the combustion seemed to take place in the fire-box without sufficient flame to carry the heat into the kiln chamber, so that while the former was incandescent with excessive heat, the latter was comparatively cool. Gas analyses showed that conditions in the kiln approached reduction, although the ware burned showed only a slight trace of it and was in general a good saleable product.

The fourth burn was made after a rearrangement of burners and firebox according to Fig. 3.

According to this method, the jet of oil was made to impinge upon a fire brick (A) about half way down the fire box, and a flue (C) was built in to conduct air to the point of maximum temperature. With this arrangement, a much better distribution of heat was obtained. The air preheated by passing through a flue (C) was drawn into the firebox and served to assit combustion and to act as a conveyor by means of which the heat was carried into the kiln chamber. Two kilns were burned under these conditions, but it was found that, while the heat in the firebox was not so intense as it had been in the preceding burns, the piers supporting the floor near the fireboxes were greatly affected by the heat, and during the second burning settled considerably.

TRANS. AM. CER. SOC. VOL. X - GRIFFIN.

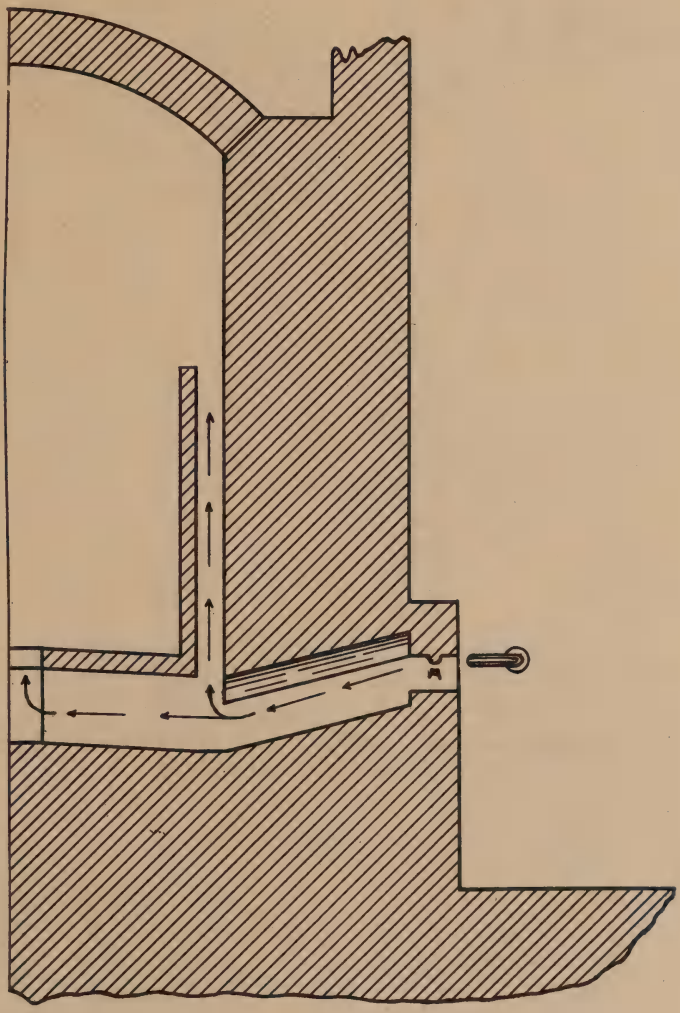

FIG. 2.

TRANS. AM. CER. SOC. VOL. X. GRIFFIN

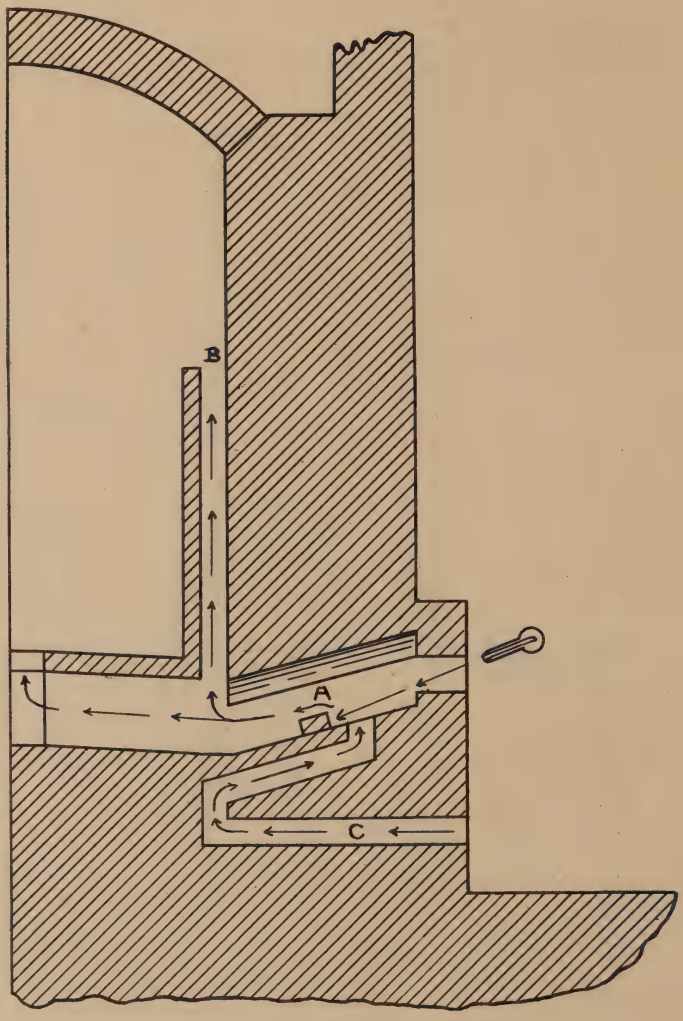

FIG. 3.

A third arrangement is readily explained by Fig. 4.

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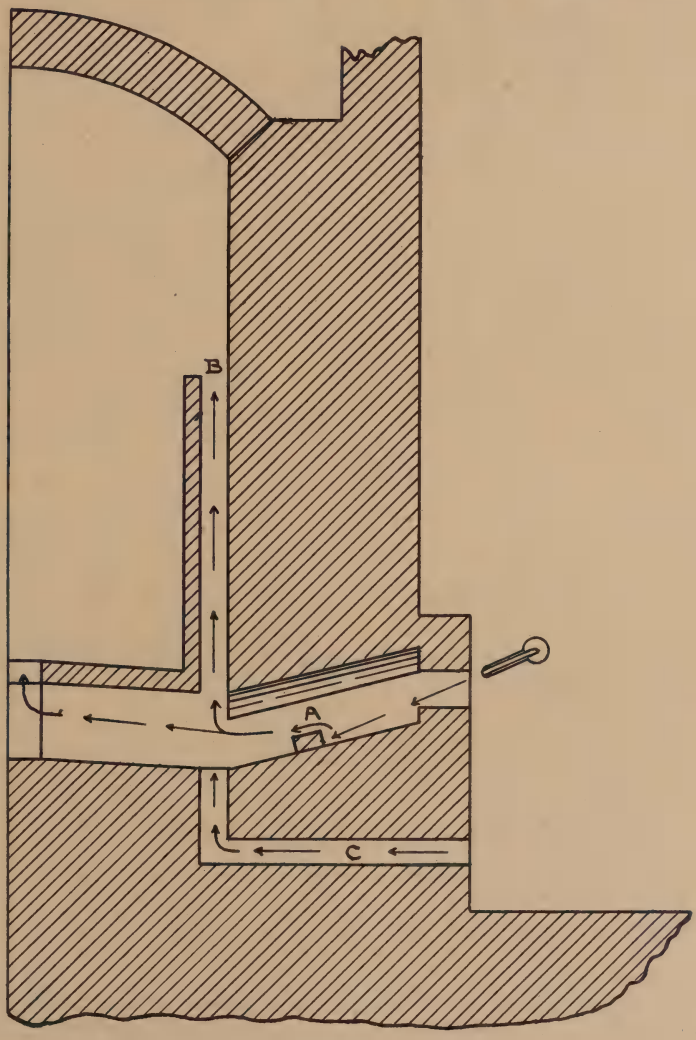


FIG. 4.

By this method the air current was conducted to the point shown to be the most affected by the two preceding firings and very good results were obtained, both as to distribution of heat and condition of the ware. Two burns were made with this arrangement without damage to the kiln from excessive heat.

The following tables give the cost of fuel and labor for seven kilns fired with crude oil and seven kilns of the same size fired with anthracite coal:

KILNS BURNED WITH CRUDE OIL.

Burn No.	Arrangement No.	Hours Burning	Callons of Oil.	Average Gallons per hr.	Cost of Oil.	Cost of Labor.
1	1	32	400	12.50	$14.00	$7.20
2	1	32	450	14.06	15.75	7.20
3	1	31	483	15.50	16.91	6.98
4	2	27	386	14.33	13.51	6.08
5	2	30	392	13.06	13.72	6.75
6	3	31	430	13.87	15.05	7.98
7	3	33	426	12.90	14.91	7.43
Average		30.85	423.8	13.74	$14.83	$7.08

KILNS BURNED WITH ANTHRACITE COAL.

Burn No.	Hours Burning.	Pounds of Coal.	Average Pounds per Hour	Cost of Coal	Cost of Labor.
1	42	4435	105	$ 8.65	$ 9.45
2	52	5555	111	10.74	11.25
3	42	4547	108	8.84	9.45
4	51	5376	105	10.46	11.48
5	49	4121	84	8.00	11.03
6	45	5130	114	9.97	10.13
7	43	4122	96	8.03	9.68
Average	45	4755	103	$ 9.24	$10.35

The fuel costs in the above tables are figured on oil at $0.035 per gallon and anthracite coal at $4.35 per gross ton.

A study of these tables develops the fact that one gallon of crude oil is equivalent in heating value to 11.22 pounds of coal. Since the weight of one gallon of this oil is 7.18 pounds, this value in units of weight is 1 to 1.562. From this proportion, and their costs per pound, the costs of equivalent heating values of oil and coal are found to be in the ratio of 1.6 to 1, which shows oil, under the conditions of this test, to cost 60% more than anthracite coal.

By using oil, the time of burning and hence the labor for firing is reduced by about 33%. Also the cost of cleaning fire-boxes and removing ashes, which adds about 45c to the labor charge for coal-fired kilns of this size, would be eliminated.

These figures combined give us the following totals for fuel and labor:

Oil-fired kilns	$21.91
Coal-fired kilns	20.04
	$1.87

This saving by using coal would, of course, be proportionally greater for larger kilns, as the labor does not increase with the size of kiln at the same rate as the fuel consumption.

Repairs to fire-boxes would probably be less in oil-fired kilns than in coal-fired, as breaking the clinker from the linings in the latter would shorten their life somewhat; and the cost of unloading and handling fuel would also be slightly decreased if oil were used, but these two advantages would be more than offset by the difference in cost of fuel of the two systems.

These experiments have shown the fuel-oil system to have the following advantages:

1. Better control of fires.
2. Shorter burns possible, and consequent reduction in the cost of labor for firing.
3. Cleaning of fire-boxes eliminated and repairs on them reduced.

4. Reduction in cost of handling fuel.

On the other hand, the increase in quality of ware was not sufficient to warrant the expense of installing and operating this system, with the cost of crude oil as a fuel 60% higher than anthracite coal, at the Norton Company's plant.

DISCUSSION.

Mr. Applegate: I will ask whether Mr. Griffin has taken into consideration the increased kiln capacity?

Mr. Griffin: No; I have not taken that into consideration for the reason that we had at that time sufficient kiln room to more than handle our products under the best conditions and with the slowest burns we could possibly make. I have not figured that into the relative cost.

MY EXPERIENCE WITH CRYSTAL GLAZES.

BY

Dr. W. Pukall, Bunzlau, Silesia.

From the time of our first knowledge of crystalline and partly crystalline glazes, there has been maintained an active interest in this attractive and charming subject. Ceramists who make an effort to not only meet the general demand of the ceramic market, but to devote some time to the further development of the "Fire-Art" as well, are constantly engaged in the perfection of this splendid agency for the decoration of ceramic products.

It is not, however, merely for the sake of creating a new decorative process for ceramic wares that so much work is being done along this line. The purchasing public is as yet indifferent to this decoration, because it understands it so little. Quite a different motive urges on research along this line. It is rather the irresistable charm exercised by that mysterious force of nature upon man, that force which is able to isolate chemical substances before our very eyes, from matter in an apparently chaotic state, and to do this according to exact and definite laws. Whoever has had occasion to make a study of these laws, and to observe the wonderful effects of this formative force; whoever, with interest at its highest tension has followed the first beginning and the gradual or rapid development of splendidly formed crystals before his very eyes in the laboratory, will have experienced this charm and will understand me.

Such observations suggest the question concerning the why and wherefore, that is, a question concerning the character and principal causes of these processes, but the answer to the question will undoubtedly be withheld from even the acutest human minds for a long time to come. We have no other choice, therefore, than to be content to

smooth the way for the proofs of the process of crystallization. Work along these lines is quite sufficient, however, to not only give the greatest satisfaction and contentment from the work itself, but also, if the work be successful, to delight the eye of him who appreciates beauty, with magnificent forms not built by the hand of man, and with colors not reproducible on the painter's canvas. Imitation of natural crystals is nothing new. These crystals have never been produced, however, in such charming forms as ceramic art has recently been enabled to conjure forth. Crystal glazes have thus become one of the most beautiful, peculiar and at the same time, distinguished means of ceramic decoration, and in this field form a new creation which may well take its place by the side of the most brilliant achievements of former times.

If crystalline glazes appeal to the general public as odd or bizarre, that impression will disappear after acquaintance as surely as does the snow disappear before the rays of the sun. It may be asserted with certainty that this "fire-art" will prove itself the means by which ceramics will make many a new friend.

It is not the purpose of this paper to give either a historical sketch of the development and progress of crystal glazes or to make scientific deductions from certain phenomena presented by them. It is the writer's purpose to make his own experiences more generally known, not only that he may incite others to further work along these lines, but also that he may be incited himself by others. He hopes that this may result in the promotion of this great branch of artistic activity.

The first crystal formation on ceramic products noticed by the writer was on porcelain vases from a famous Danish porcelain factory. Later I noticed crystals in the glaze of a rather old, small Japanese porcelain vessel. A real crystal glaze that appeared in the market somewhat later was subjected to analysis, but the results did not lead me to any satisfactory conclusions This plan was then abandoned entirely and independent experiments substi-

tuted. I used high grade stoneware as the body in all experiments, which proved to be excellently adapted to the purpose. I will have more to say about this farther on. The chief agencies used for the production of crystals were zinc oxide and titanium oxide, the latter in the form of rutile. Although manganese oxide and cobalt oxide also incline to crystal production, the two first mentioned were used exclusively, because they gave better promise of results. After the first rutile crystals appeared, and gave much promise, the zinc oxide crystals were entirely abandoned. From my personal experience, they are indeed more easily obtained, but far less beautiful. The zinc crystals have since been produced in various places so abundantly, and have been described with such detail, that I shall omit all comment on the results of my few experiments and confine myself to the less known, extremely beautiful pure rutile crystals.

I wish to state at the very beginning that my work in this line was confined to comparatively small articles. On the one hand this was imperative owing to the small dimensions of the kilns in the Bunzlau Ceramic School, and on the other hand, I believe I have found it to be generally true that the artistic charm of ceramic products of whatever nature decreases pretty much as the square of the size increases. The largest vessels had a height of only 30 cm., with a proportionate diameter.

The first experiment was to add rutile by small increments up to 15% to a known white ware glaze of not too refractory nature. This white ware glaze was of the ordinary fritted type and was fritted at the usual temperature. As a rule, nothing in particular was manifested in this operation, only that a large addition of rutile caused a matteness of the glaze, accompanied by the separation of distinctly marked crystals. Generally also, not much change was to be noted with increased temperature. However, it was observed that on the addition of coarse-grained rutile, a crystallization took place proceeding from the coarse granules as nuclei. This seemed to justify greater

hopes, but still it did not produce any satisfactory result. Rutile in quantities up to 15% was now fritted together with various glaze fritts, pulverized and fused on as a glaze, with and without other additions. In several cases, very acceptable results were obtained by this procedure, as for instance in the glazes containing zinc and having the molecular formulæ as follows:

I.

$$\left.\begin{matrix}0.5\ PbO\\0.2\ CaO\\0.1\ K_2O\\0.2\ ZnO\end{matrix}\right\} \quad 0.1\ Al_2O_3 \quad \left\{\begin{matrix}2.00\ SiO_2\\0.5\ TiO_2\end{matrix}\right.$$

II.

$$\left.\begin{matrix}0.5\ PbO\\0.2\ CaO\\0.3\ ZnO\end{matrix}\right\} \quad 0.2\ Al_2O_3 \quad \left\{\begin{matrix}1.8\ SiO_2\\0.4\ TiO_2\end{matrix}\right.$$

These glazes produced by these batch weights

I.

55.6	Feldspar
84.0	Sand from Hohenbocka
41.1	Rutile
114.2	Red Lead
20.0	Marble Dust
16.2	Zinc Oxide
331.1	

II.

51.6	Zettlitz Kaolin, raw
84.0	Sand from Hohenbocka
32.9	Rutile
114.2	Red Lead
20.0	Marble Dust
24.3	Zinc Oxide
327.0	

These results are quite acceptable. After the compounding as indicated above, they were lightly fritted, pulverized and, without any further additions, were fused in the high temperature muffle on a piece of fine stone-ware body at cone 7. Both showed an almost too prolific crystallization as follows:

(1) Cabbage shaped crystals in an opaque ivory-colored groundmass, radiating from a common center and consisting of formations varying in appearance from that of coarse needles down to fine and even most delicate featherlike forms.

(2) Compact needles, in a grayish-violet, semi-transparent groundmass, intertwining and jumbled together, and of a strongly matted appearance, showing in only a few places star-shaped crystals whose ends are of a fibrous structure. This latter peculiarity increased directly as the amount of zinc present increased.

Although a great step forward has been made in the attainment of these results, they were not yet satisfactory from the view point of decorative art, especially since it was also observed that the various metal oxides used for coloring purposes had a greatly varying effect, sometimes aiding and sometimes retarding the tendency to crystallization. Among those that aid the crystallization must be counted first cupric oxide, then manganese oxide, and perhaps also iron and uranium oxide. All the others behaved in a not very favorable manner and could be used only in rather small quantities. It was also shown that the colorless crystal glazes, which are really the chief ones for decorative purposes, could not always be utilized directly in the production of colored glazes but that they had to be worked over. This turned all the experiments into new channels in which the work was continued with highly satisfactory results, especially since the method of preparing the glazes was thereby considerably simplified.

An alkaline fritt adapted to whiteware glazes having the following composition was melted:

A.

$$\left.\begin{matrix} 0.50\ PbO \\ 0.15\ K_2O \\ 0.15\ Na_2O \\ 0.10\ CaO \\ 0.10\ BaO \end{matrix}\right\} 0.10\ Al_2O_3 \left\{\begin{matrix} 2.70\ SiO_2 \\ \\ 0.30\ B_2O_3 \end{matrix}\right. = 349.0 \text{ Comb. Wt.}$$

The batch weight was as follows:

A'.

10.10	Potassium Nitrate
55.60	Feldspar
57.30	Borax, crystallized
10.00	Marble Dust
19.74	Barium Carbonate (Witherite)
114.16	Red Lead
126.00	Sand from Hohenbocka
392.90	

This fritt, after fusion to a transparent glass, together with the addition of rutile, various quantities of an unfritted mixture (a) and of various metallic oxides, served as the starting point of a whole series of experiments. The composition of (a) was:

(a).

$$\left.\begin{matrix} 0.5\ CaO \\ 0.4\ MgO \\ 0.1\ K_2O \end{matrix}\right\} 0.4\ Al_2O_3\ \ 1.6\ SiO_2 = 229.8 \text{ Comb. Wt.}$$

and the batch weight:

(a').

50.0	Marble Dust
55.6	Feldspar
66.6	Zettlitz Kaolin, ignited
24.0	Sand from Hohenbocka
33.6	Magnesite

Only the most successful member of this series will be mentioned here.

It consisted of a mixture of:

100.0	Glaze Frit (A)
100.0	Glaze, raw base
30.0	Rutile
12.0	Copper Oxide
242.0	

which corresponds to the formula:

$$\left.\begin{matrix} 0.282\ CaO \\ 0.200\ MgO \\ 0.173\ CuO \\ 0.164\ PbO \\ 0.099\ K_2O \\ 0.049\ Na_2O \\ 0.033\ BaO \end{matrix}\right\} 0.232\ Al_2O_3 \left\{\begin{matrix} 1.687\ SiO_2 \\ 0.430\ TiO_2 \\ 0.097\ B_2O_3 \end{matrix}\right.$$

Except with the copper oxide, and perhaps also the manganese oxide, this glaze did not yield any specially serviceable effects. At a temperature of cone 7 there were developed from a light grayish green groundmass, exceedingly delicate, silver-gray fanshaped forms, arranged in sets of two each, with the handles or stems towards each other. Occasionally, there are four in a set, arranged in the form of a cross. By the continued expansion of the fan surfaces, these finally met and touched their neighbors. In this manner there arose groups of crystal flowers of various size, then again large vacant spaces, or spaces showing an incipient crystallization. In some instances the whole vessel was covered uniformly with crystals. In such a case the crystals were deficient in delicacy of structure. In those cases, especially where the glaze was applied in thin layers or where it drained off because of too high temperature, fan-shaped crystals just described were frequently intertwined with others that were compact, needle-shaped, and often radiated from a common center, reminding one of small tufts of grass. As a rule the individual crystal flowers remain small in size and attain a diameter of 0.5—0.8 mm. or less. If they are otherwise perfect, this does not detract from their charming appearance.

This glaze was, however, abandoned in the effort to obtain a stronger development of crystals and, above all, a greater variety of color shades, especially since it had been shown that with the fritt and rutile without the raw base glaze (a) larger and more regularly developed crystal stars could be obtained. Thus, for instance, very beautiful,

delicately-fibred crystals were obtained by using the following mixture:

100	Glaze Fritt A
15	Rutile
6	Cupric Oxide
121	

According to the system of writing formulæ devised by Seger, this appears as follows:

$$\left.\begin{array}{l} 0.079\ BaO \\ 0.079\ CaO \\ 0.118\ K_2O \\ 0.119\ Na_2O \\ 0.209\ CuO \\ 0.396\ PbO \end{array}\right\} 0.079\ Al_2O_3 \left\{\begin{array}{l} 2.137\ SiO_2 \\ 0.578\ TiO_2 \\ 0.237\ B_2O_3 \end{array}\right.$$

These crystals appeared singly, or if in groups, not very crowded, were silverhued, of various sizes but not over 8-10 mm. in diameter, and appeared on a grayish green to a vivid dark green ground. This glaze was developed at a temperature of cone 4, at the greatest advantage because of its greater percentage of boric acid and small alumina content. This temperature proved to be too low for the fine stoneware body described farther on, so that it caused an occasional fracture by the cracking of vessels on cooling. The beauty of the glaze required an adjustment of the body to the temperature mentioned, and this was done without difficulty.

Of the other coloring oxides, manganese oxide was the only one that yielded somewhat serviceable results. The most beautiful results were obtained by the simultaneous employment of the oxides of copper and manganese, according to the following batch weight:

100	Glaze Fritt (A)
15	Rutile
6	Copper Oxide
3	Manganese Hydroxide
124	

having as a molecular formula

$$\left.\begin{matrix} 0.396\ PbO \\ 0.209\ CuO \\ 0.119\ Na_2O \\ 0.079\ BaO \\ 0.079\ CaO \\ 0.118\ K_2O \end{matrix}\right\} \quad \begin{matrix} 0.079\ Al_2O_3 \\ 0.039\ Mn_2O_3 \end{matrix} \quad \left\{\begin{matrix} 2.137\ SiO_2 \\ 0.518\ TiO_2 \\ 0.237\ B_2O_3 \end{matrix}\right.$$

The most beautiful development of the glaze is obtained at temperatures between cones 4 and 7. From an olive colored ground there are developed numerous fine greenish-brown star-shaped crystals. As in all cases already described and yet to be described, they do not injure the lustre of the glaze. In this case, they have spread out until their respective edges meet, forming areas of irregular polygonal shape, bounded by straight lines, while in the glaze just described, containing copper oxide only, the crystals are smaller and generally separated by uncrystallized areas. The new crystallization, however, does not injure the beauty of the total effect in the least. The diameter of the individual star crystal is still below 1 cm., which however does not effect their decorative value.

However, the experiments took quite a different turn after it had been observed that the fluxing effect of titanim oxide, which originally suggested the possibility of crystal formation, may be considerably increased at times by inconsiderable additions of compounds of vanadium, tungsten and molybdenum. This makes it more than possible to obtain larger crystals which leads to more beautiful effects. But while there has been much effort expended in obtaining larger-sized crystals, the larger size is not always desirable. Crystals of 5 cm. diameter and even larger were obtained. Generally, however, they are smaller, because they impede each other's development. By far the most favorable results are obtained by the addition of vanadium compounds, and among these vanadate of ammonium is the best. Although soluble in water, it can be added to the glaze slip (which must not be too thin) before it is applied, and ground up with it. By being partially dis-

solved in the water it comes into a closer contact with the other constituents of the glaze. In the case of tungsten and molybdenum, the ammonium salts may be used to advantage, but the acid anhydrides were the ones chiefly used. Special attention must be called to the fact, however, that the effects of the compounds named was not equally good for all glaze mixtures. It may happen that if one of the three acts favorably upon the crystallization, the other two will effect it unfavorably.

It was now necessary to counteract an evil that is connected with this greater fluxing of crystal glazes. This evil consisted in the almost complete flowing off of the glaze from the vessel, forming the most beautiful crystals on the support or on muffle bottom. I tried two methods of doing this. One of them, that had already been used elsewhere, consisted in attaching on the top edge of the neck of the vessel to be decorated, a ring having nearly the same diameter, or at least having the same diameter at the point of contact. This ring should be made of the same body and put on either loosely, or made to adhere by a mixture of kaolin and sand, or it should be left connected with it from the very beginning. This is especially applicable to cast pieces. The crystal glaze is now applied to this attachment irregularly and in large quantities. After it has attained the proper fluidity it flows from this attached ring over the vessel, and if the quantity was properly estimated, it develops there the most beautiful crystals. By means of the section-cutting disc the attachment is now cut off and the cut surface smoothed by polishing.

Those who have no such cutting apparatus will do better by using the following method, because the striking or breaking off of the attachment by means of tongs often means the loss of the vessel itself. The method just described often results in leaving large patches of the vessel without any glaze on it, because the glass flux running down from the upper tube did not spread properly or else separated into a few thin streaks. This can be avoided by first applying a regular ground glaze, whose color is care-

fully selected. This ground glaze must not crystallize at all or but little, but otherwise may contain a small percent of rutile and coloring oxide, if the desired shade requires it. The rutile may, however, also be disregarded as will be shown farther on. This ground glaze which, of course, contains neither vanadium, nor molybdenum nor tungsten, and for this purpose ought to be somewhat more refractory than that of the real crystal glaze applied over it.

If, while perhaps still in a porous condition, a stream or drop of the less viscous crystalline glaze begins to flow over the more viscous underglaze, the former is obstructed in its course, forced to spread in all directions, and finally after reinforcement have ceased to come, to sink into the ground glaze. The whole process may be plainly observed in the muffle. The results of this method are of a more or less accidental nature. Surfaces that are covered or not covered or only sparsely covered with crystals, appear variously colored, so that this method gains considerably in interest and makes it possible to attain a great variety of effects that are also exceedingly charming.

The composition of the ground or under-glaze is a matter of little import, especially when its melting point is much higher than that of the crystal glaze. Glazes whose melting point was cone 4 were found to be quite serviceable. If the melting point is higher than cone 4, then as a rule the crystal glaze shivers, perhaps not immediately, but after a little while.

The second method makes the use of an attached ring, from which the melted crystal glaze runs down onto the vessel, unnecessary, at least in those cases in which refractory ground glazes are used. The ground glazes, used in almost all cases in an unfritted condition, offer sufficient resistance to prevent the too rapid down-flow of the crystal glaze. The crystal glaze is spread irregularly at the very top of the neck of the vessel, and from there it is allowed to run down.

In the following I give some mixtures of ground glazes together with some crystal glazes adapted to them, with

which I had very satisfactory results. The ground glazes are:

B	100	Glaze Fritt (A)
	3	Cobalt Oxide
	10	Rutile
	113	

C	100	Glaze Fritt (A)
	3	Manganese Oxide
	10	Rutile
	113	

In the Seger formula they are as follows:

B	0.439 PbO 0.132 Na_2O 0.132 K_2O 0.123 CoO 0.088 CaO 0.088 BaO	0.088 Al_2O_3	0.263 B_2O_3 0.383 TiO_2 2.369 SiO_2	

C	0.50 PbO 0.15 Na_2O 0.15 K_2O 0.10 CaO 0.10 BaO	0.066 Mn_2O_3 0.100 Al_2O_3	0.300 B_2O_3 0.437 TiO_2 2.700 SiO_2	

These ground glazes when colored by other metallic oxides may be increased at pleasure, but the two mentioned above, and especially C, proved themselves quite serviceable. I used with them the following exterior or "flow glazes:"

6		7	
100	Glaze Fritt (A)	100	Glaze Fritt (A)
3	Cobalt Oxide	3	Manganese Oxide
2	Ammonium Vanadate	2	Ammonium Vanadate
15	Rutile	15	Rutile
120		120	

8		9	
100	Glaze Fritt (A)	100	Glaze Fritt (A)
3	Uranium Oxide	3	Copper Oxide
2	Ammonium Vanadate	2	Ammonium Vanadate
15	Rutile	15	Rutile
120		120	

This series can be increased at pleasure by the introduction of other coloring oxides, except chromium oxide. They may be increased or decreased in quantity, several oxides may be introduced at the same time, or they may be mixed, one with the other, in various ratios. Those mentioned above yielded the best results however, and 7 and 9 were especially satisfactory. The others will be found important when we later come to speak of reductions and infiltrations.

To permit a comparison between the two ground glazes, the Seger formulæ of the two crystal glazes 6 and 7 are given below:

$$6 \quad \left.\begin{matrix} 0.437\ PbO \\ 0.131\ Na_2O \\ 0.131\ K_2O \\ 0.127\ CoO \\ 0.087\ CaO \\ 0.087\ BaO \end{matrix}\right\} 0.087\ Al_2O_3 \left\{\begin{matrix} 2.357\ SiO_2 \\ 0.571\ TiO_2 \\ 0.262\ B_2O_3 \\ 0.026\ V_2O_5 \end{matrix}\right.$$

$$7 \quad \left.\begin{matrix} 0.50\ PbO \\ 0.15\ K_2O \\ 0.15\ Na_2O \\ 0.10\ CaO \\ 0.10\ BaO \end{matrix}\right\} \left\{\begin{matrix} 0.066\ Mn_2O_3 \\ 0.087\ Al_2O_3 \end{matrix}\right. \left\{\begin{matrix} 2.700\ SiO_2 \\ 0.654\ TiO_2 \\ 0.300\ B_2O_3 \\ 0.030\ V_2O_5 \end{matrix}\right.$$

As may be seen from the above, the flow crystal glazes differ from those applied directly on the body in having a smaller quantity of titanic and vanadic acid.

With the use of a new glaze fritt, which proved to be still better adapted to the production of crystal glazes, experiments along this line entered upon a new stage of development. Here is the formula:

$$\left.\begin{matrix} 0.5\ PbO \\ 0.2\ Na_2O \\ 0.2\ CaO \\ 0.1\ K_2O \end{matrix}\right\} 0.1\ Al_2O_3 \left\{\begin{matrix} 2.5\ SiO_2 \\ 0.2\ B_2O_3 \end{matrix}\right. = 318.7 \text{ Comb. Wt.}$$

The batch weight being:

10.60	Soda, calcined
38.20	Borax, crystallized
55.60	Feldspar
20.00	Marble dust
114.17	Red lead
114.00	Sand from Hohenbocka, or Quartz
352.57	

The following mixtures were tried:

10

100	Glaze Fritt D
5	Copper Oxide
5	Ammonium Vanadate
15	Rutile
125	

11

100	Glaze Fritt D
5	Manganese Oxide
5	Ammonium Vanadate
15	Rutile
125	

12

100	Glaze Fritt D
1	Cobalt Oxide
5	Ammonium Vanadate
15	Rutile
121	

13

100	Glaze Fritt D
1	Uranium Oxide
5	Ammonium Vanadate
15	Rutile
121	

14

100	Glaze Fritt D
2	Iron Oxide
5	Ammonium Vanadate
15	Rutile
122	

Numerous others were also tried, but they did not produce even approximately the results attained by those given above. By far the best results were produced in this instance also by the oxides of copper or manganese, or the two batches 10 and 11 containing both, or mixtures of them in varying ratios. The others, so far as direct results for decorative purposes are concerned, play but a minor part, but they will doubtless prove themselves worthy of notice later. For the purpose of comparison with preceding crystal glazes, I have expressed the glazes 10 and 11 in terms of the Seger formula:

10,

$$\left.\begin{matrix} 0.417\ PbO \\ 0.167\ CuO \\ 0.167\ CaO \\ 0.166\ Na_2O \\ 0.083\ K_2O \end{matrix}\right\} 0.082\ Al_2O_3 \left\{\begin{matrix} 2.083\ SiO_2 \\ 0.498\ TiO_2 \\ 0.167\ B_2O_3 \\ 0.057\ V_2O_5 \end{matrix}\right.$$

11,

$$\left.\begin{matrix} 0.500\ PbO \\ 0.200\ CaO \\ 0.200\ Na_2O \\ 0.100\ K_2O \end{matrix}\right\} \left\{\begin{matrix} 0.100\ Al_2O_3 \\ .101\ Mn_2O_3 \end{matrix}\right. \left\{\begin{matrix} 2.500\ SiO_2 \\ 0.598\ TiO_2 \\ 0.200\ B_2O_3 \\ 0.068\ V_2O_5 \end{matrix}\right.$$

It will be seen by a comparison that these crystal glazes do not differ very much in chemical composition from those previously given, and yet the results in the two cases were entirely different, and in the latter were even incomparably more beautiful.

These glazes may also be used with or without a ground glaze, but it is better to use one. The composition of these ground glazes and their coloring is a matter of little importance unless it happens that they do not harmonize in their color tones. A very successful ground glaze was obtained by the following mixture:

100	Glaze Fritt A
100	Mixture containing Iron Oxide (F)
12	Rutile
212	

The mixture containing iron oxide (F) is an imitation of a mineral (diorite). I have used the mixture for other purposes. It corresponds to the formula:

$$\mathrm{F}\quad \left.\begin{matrix}0.507\ \mathrm{CaO}\\ 0.348\ \mathrm{MgO}\\ 0.145\ \mathrm{K_2O}\end{matrix}\right\}\ \left\{\begin{matrix}0.522\ \mathrm{Al_2O_3}\\ 0.225\ \mathrm{Fe_2O_3}\end{matrix}\right\}\ 2.019\ \mathrm{SiO_2} = 284.33\ \text{Comb. Wt}$$

and is obtained by the batch weights: :

80.62	Feldspar
19.35	Zettlitz Kaolin, raw
41.70	Sand from Hohenbocka
36.00	Iron Oxide
50.70	Marble Dust
29.23	Magnesite
335.52	

This mixture of fritt, iron stain and rutile was used without further fritting, and for this reason carbon dioxide and water of hydration must be considered when calculating into other batches. The above mentioned ground glaze accordingly corresponds to the Seger formula:

$$\mathrm{E}\quad \left.\begin{matrix}0.307\ \mathrm{CaO}\\ 0.245\ \mathrm{PbO}\\ 0.177\ \mathrm{MgO}\\ 0.148\ \mathrm{K_2O}\\ 0.074\ \mathrm{Na_2O}\\ 0.049\ \mathrm{BaO}\end{matrix}\right\}\ \left\{\begin{matrix}0.310\ \mathrm{Al_2O_3}\\ 0.115\ \mathrm{Fe_2O_3}\end{matrix}\right\}\ \left\{\begin{matrix}2.501\ \mathrm{SiO_2}\\ 0.257\ \mathrm{TiO_2}\\ 0.147\ \mathrm{B_2O_3}\end{matrix}\right.$$

On comparing this ground glaze with the two given above, it will be seen that one may move within rather wide bounds so far as the compositions of these glazes is concerned. It was discovered later that lead oxide, boric acid and not even titanic acid are necessary, but that every colored or uncolored whiteware or stoneware glaze can be coated with crystal glaze. With particularly refractory ground glazes however crazing or shivering may result. Very peculiar effects, with an especially strong development of crystal stars were obtained on a ground glaze having the following composition:

$$G \quad \left.\begin{matrix} 0.627\ CuO \\ 0.224\ CaO \\ 0.075\ MgO \\ 0.074\ K_2O \end{matrix}\right\} \quad 0.149\ Al_2O_3 \quad \left\{\begin{matrix} 1.306\ SiO_2 \\ 0.124\ TiO_2 \end{matrix}\right.$$

according to the batch weights: :

53.49	Copper Oxide
22.40	Marble Dust
6.30	Magnesite
41.14	Feldspar
19.35	Zettlitz Kaolin, raw
42.72	Sand from Hohenbocka
9.92	Rutile
195.32	

In this case, the ground-glaze, which likewise served other purposes originally, was first fused on separately, but this is not absolutely necessary. It was not covered with the crystal glaze No. 10, containing copper oxide, until the second fire. The results of this showed for the first time an occasional absence of crystals. In their place, there appeared a surface which showed a radiant dirty green color in direct light, but in reflected rays showed an intensely luminous, bright green, phosphorescent light, which gained for it the name "catseye glaze." This will be referred to again later on.

A most peculiar effect was obtained on the following stoneware glaze (H), free from boric acid and titanic acid, used as a foundation for crystal glazes:

H	0.7 CaO 0.2 K_2O 0.1 MgO	0.4 Al_2O_3	3.5 SiO_2

This flows smooth even at cone 4, and corresponds to the following batch:

111.2	Feldspar
51.6	Zettlitz Kaolin, raw
114.0	Sand from Hohenbocka
70.0	Marble Dust
8.4	Magnesite
355.2	

Ground and crystal glazes were, with but few exceptions (see above), always fused in one and the same fire. In dipping, the biscuited vessel was first covered with the ground glaze (H) and then the crystal glaze was applied in an irregular manner on the upper part of the vessel and on the top of the ground glaze.

Along with the experiments just described others were being carried on in the laboratory of the Bunzlau Ceramic Technical School, some of which produced remarkable results as shown below. In one case, the following fritt was used:

I	0.367 PbO 0.257 CaO 0.179 K_2O 0.163 Na_2O 0.043 MgO	0.300 Al_2O_3	3.570 SiO_2 0.326 B_2O_3

This was used on a ground glaze having the following formula:

J	0.2 MgO 0.3 CaO 0.5 K_2O	0. Al_2O_3	5.0 SiO_2

The batches for these two glazes are respectively:

I		J	
99.52	Feldspar	278.0	Feldspar
31.22	Zettlitz Kaolin, raw	16.8	Magnesite
135.24	Sand from Hohenbocka	30.0	Marble Dust
62.27	Borax, crystallized	25.8	Zettlitz Kaolin, raw
83.77	Red Lead	108.0	Sand from Hohenbocka
25.70	Marble Dust	458.6	
2.80	Magnesite		
440.58			

From a large number of experiments, only a selection of those that gave the best crystalline glazes will be mentioned here. They differ from those previously mentioned in that they contain molybdic acid and iron oxide along with titanic acid, and the oxides of copper and manganese. This, on the whole, was an improvement. Vanadic acid was abandoned entirely. The colorless ground glaze was completely covered with crystal glaze in every case. This developed the fact that the crystal glazes containing iron oxide are developed better without a ground glaze, but that the others require one. The following mixtures proved to be best adapted to the purpose:

15

100	Glaze Fritt I
13	Rutile
2	Molybdic Acid (anhydrous)
10	Copper Oxide
125	

16

100	Glaze Fritt I
13	Rutile
2	Molybdic Acid (anhydrous)
10	Copper Oxide
3.5	Iron Oxide
128.5	

17

100	Glaze Fritt I
13	Rutile
2	Molybdic Acid (anhydrous)
10.0	Copper Oxide
1.5	Iron Oxide
1.5	Manganese Oxide
127.5	

18

100	Glaze Fritt I
13	Rutile
2	Molybdic Acid (anhydrous)
10	Copper Oxide
4	Manganese Oxide
129	

The addition of molybdic acid tended to develop crystal stars that at times attained a diameter of from 20 to 30 mm. This tendency on the part of molybdic acid was found to be very advantageous provided the crystals did not become too large. The fundamental color with 15 was a vivid green, with 16 and 17 more brownish, and with 18 yellowish green. In the latter, which was the most beautiful, the crystal stars at times showed a blueish fringe. With others the above mentioned phosphorescent glow was evident in reflected light.

For the sake of comparison, the Seger formulæ of these four glazes are herewith given: :

15

$$\left.\begin{matrix}0.330\ CuO\\0.246\ PbO\\0.172\ CaO\\0.120\ K_2O\\0.109\ Na_2O\\0.023\ MgO\end{matrix}\right\}\ 0.201\ Al_2O_3\ \left\{\begin{matrix}2.392\ SiO_2\\0.036\ MoO_3\\0.218\ B_2O_3\\0.427\ TiO_2\end{matrix}\right.$$

16

$$\left.\begin{matrix}0.330\ CuO\\0.246\ PbO\\0.172\ CaO\\0.120\ K_2O\\0.109\ Na_2O\\0.023\ MgO\end{matrix}\right\}\ 0.201\ Al_2O_3\ \left\{\begin{matrix}2.392\ SiO_2\\0.427\ TiO_2\\0.218\ B_2O_3\\0.036\ MoO_3\end{matrix}\right.\ +0.057\ Fe_2O_3$$

17

$$\left.\begin{matrix}0.330\ CuO\\0.246\ PbO\\0.172\ CaO\\0.120\ K_2O\\0.109\ Na_2O\\0.023\ MgO\end{matrix}\right\}\ 0.201\ Al_2O_3\ \left\{\begin{matrix}2.392\ SiO_2\\0.427\ TiO_2\\0.218\ B_2O_3\\0.036\ MoO_3\end{matrix}\right.\ +0.067\ Mn_2O_3$$

18

$$\left.\begin{matrix}0.330\ CuO\\0.246\ PbO\\0.172\ CaO\\0.120\ K_2O\\0.109\ Na_2O\\0.023\ MgO\end{matrix}\right\}\ \left\{\begin{matrix}0.201\ Al_2O_3\\0.025\ Fe_2O_3\\0.025\ Mn_2O_3\end{matrix}\right.\ \left\{\begin{matrix}2.392\ SiO_2\\0.427\ TiO_2\\0.218\ B_2O_3\\0.027\ MoO_3\end{matrix}\right.$$

The crystal glazes containing no iron oxide are, of course, not restricted to the above mentioned ground glaze J. Any other may be used, provided it is more refractory than the crystal glaze.

The investigation of titanium crystal glazes was taking another step forward in an independent parallel piece of work which was carried on in the laboratory of the Bunzlau Ceramic Technical School. This proceeded from a composition similar to glaze I, that is to say, a glaze having the following composition:

$$\mathbf{K}\ \left.\begin{matrix}0.36\ PbO\\0.25\ CaO\\0.17\ Na_2O\\0.12\ K_2O\\0.10\ MgO\end{matrix}\right\}\ 0.28\ Al_2O_3\ \left\{\begin{matrix}3.50\ SiO_2\\0.34\ B_2O_3\end{matrix}\right.\ = 382.46\ \text{Comb. Wt.}$$

of which the batch weight is

8.40	Magnesite
66.72	Feldspar
1.28	Zettlitz Kaolin, raw
147.60	Sand from Hohenbocka
64.94	Borax, crystallized
25.00	Marble Dust
82.20	Red Lead
436.14	

This, however, was divided into a fritt and mill charge. For the purpose of obtaining an easily fusible fritt, the following ingredients were taken from the total charge and fritted:

77.60	Sand from Hohenbocka
64.94	Borax, crystallized
82.20	Red Lead
224.74	

This corresponds to the formula:

$$\left.\begin{matrix} 0.679\ PbO \\ 0.321\ Na_2O \end{matrix}\right\} \quad \begin{matrix} 2.440\ SiO_2 \\ 0.642\ B_2O_3 \end{matrix}$$

For the mill charge, there were used the fritt mentioned and the remainder of the ingredients, as follows:

192.22	Fritt
8.40	Magnesite
66.72	Feldspar
41.28	Zettlitz Kaolin, raw
70.00	Sand from Hohenbocka
25.00	Marble Dust
403.62	

This thoroughly ground mixtur now formed the base for numerous crystal glaze batches of which, however, only the following two, being the best, will be mentioned:

19		20	
100.00	Glaze K	100.00	Glaze K
10.80	Rutile	12.00	Rutile
10.00	Copper Oxide	10.00	Copper Oxide
2.80	Manganese Oxide	2.80	Iron Oxide, hydrous
1.32	Tungstic Acid	0.15	Tungstic Acid, anhydrous
2.00	Molybdic Acid	1.32	Manganese Oxide, hydrous
126.92		126.27	

In the Seger formula these appear as follows:

19	0.333 CuO 0.240 PbO 0.167 CaO 0.113 Na_2O 0.080 K_2O 0.067 MgO	0.187 Al_2O_3 0.048 Mn_2O_3	2.332 SiO_2 0.015 WO_3 0.037 MoO_3 0.227 B_2O_3 0.363 TiO_2
20	0.333 CuO 0.240 PbO 0.167 CaO 0.113 Na_2O 0.080 K_2O 0.067 MgO	0.187 Al_2O_3 0.017 Mn_2O_3 0.047 Fe_2O_3	2.332 SiO_2 0.403 TiO_2 0.227 B_2O_3 0.001 WO_3

Both glazes gave best results when they were burned without a ground glaze at a temperature of cone 7 in the high-temperature muffle. This is quite permissible, because they are naturally rather viscous. No. 19 is not glossy, but rather semi-subdued in appearance, and by this very fact creates a peculiar effect. On a reddish-brown ground glaze punctuated with brownish-black dots, are developed numerous crystal stars which sometimes unite to form larger groups that have a bronze-like hue. The isolated ones are sometimes surrounded by a steel gray, finely feathered ring that generally shows a somewhat fringed edge so that, as a whole, they give the impression of small flowers of the nature of sunflowers. If (20) is used as a ground glaze, and a somewhat higher temperature applied, then the glaze turns out glossy, is of chocolate brown color, and generally develops only scattered fine-fibred crystal stars with a brown center and a scarcely visible narrow, steel-gray ring.

Glaze 20 behaves quite differently, although it does not essentially differ from 19 in its chemical composition. With a successful development, which, however, does not always take place, it is to be looked upon as the most beautiful of all. It does not always show up with equal beauty, not even with conditions that are seemingly identical. In reflected light the very glossy brownish-green foundation shows a magnificent phosphorescence in every instance,

even when few or no crystal stars appear. This phosphorescence, however, varies in degree and with the different vessels. It decreases with increasing temperature, but is never absent entirely. In this foundation, bronze-colored crystals of extreme delicacy appear that have an ever changing play of colors. They generally unite at the lower part of the vessel to form larger groups, but they also appear as individuals and then attain a size up to 2 cm. diameter. Where the crystals appear in crowded groups, the gloss of the glaze is affected but little and that little is scarcely noticeable, as is the case with all other glazes. Prosphorescence in reflected light is confined to those surfaces that show no crystals.

The manner of production of the crystal glazes last described gave occasion for tests with several easily-fusible fritts with which white ware glazes, whose fusing point is not above cone 4, were used as mill charges and with the addition of rutile, copper oxide and manganese compounds together with small quantities of molybdic, tungstic and vanadic acids. These frits were tested as to their adaptability to crystal glazes and promising results were obtained, as, for instance with the fritt:

$$\left.\begin{matrix} 0.5\ PbO \\ 0.4\ Na_2O \\ 0.1\ CaO \end{matrix}\right\} 2.5\ SiO_2$$

obtained from

10.00	Marble Dust
42.40	Soda, calcined
114.08	Red Lead
115.00	Sand from Hohenbocka
281.48	

and the stoneware glaze (H) before given. There were mixed for the crystal glaze

100.0	Fritt
100.0	Stoneware Glaze H
25.3	Rutile
21.1	Copper Oxide
5.6	Iron Oxide (hydrous)
2.8	Manganese Oxidee (hydrous)
4.2	Tunstic Acid (anhydrous)
259.0	

The glaze was applied without a ground glaze. The burning temperature reached the point of cone 7. The best results, however, were obtained at the temperature of cone 9. Beautiful results were also obtained by using it as the ground glaze, and having it overflown by crystal-glaze 10. In this case the temperature of cone 7 is quite adequate.

In one instance beautiful and large crystal stars were obtained with a raw glaze having the composition

$$22 \quad \left.\begin{matrix} 0.9\ PbO \\ 0.1\ K_2O \end{matrix}\right\} 0.1\ Al_2O_3 \quad 2.0\ SiO_2$$

obtained from a mixture of

55.6 Feldspar
200.7 Lead Oxide
84.0 Sand from Hohenbocka

with the addition of 10% rutile and 2% ammonium vanadate, at a burning temperature between cones 4 and 7. On reduction, these crystals have a metallic gray appearance. No ground glaze was used.

It must be admitted that, generally speaking, the success of titanium crystal glazes depends upon a number of things of an accidental nature. It is not merely a question of the chemical composition of the glaze, as is frequently the case, e. g., in Chinese red, but the purely mechanical features play an important part, as for instance the nature of the fritt and of the admixtures. According to my experience it is not advisable to fritt in the rutile and the metal oxides. The burning apparatus, the duration of burning, draft, height of temperature, fuel and many other things are of decisive importance. It is by no means an unimportant factor, for instance, whether the same fuel is used in a moist or dry condition. It may occur that results that were easily obtained in every instance months ago, on repetition can not again be obtained. The reverse is also true. Glazes that for some reason had been rejected suddenly produce the finest effects, because some one of the factors co-operating in the results has changed meanwhile, and the change has not been observed by the experi-

mentor. Occasionally the crystallization of the same glaze will fail entirely to materialize under seemingly the same conditions, and in other cases it will occur in superabundance without any apparent cause. Occasionally the burnings will be a complete failure without any change in the glazez or the process having been consciously made. Even with good success almost every burning shows a different result, which fact is a constant stimulus to every new experiment. Although the oxides of copper and manganese, and their mixtures have as yet yielded almost the only pronounced results, there is absolutely no cause to fear monotony, especially as variety may be produced by several very simple methods of procedure, as will be shown farther on. A method for the decoration of large articles will, therefore, never be derived from the technique of titanium crystal glazes. Nor is this at all necessary, for this would be quite out of keeping with its character.

I found the fine stoneware* a very satisfactory base for all kinds of decorations produced by the agency of fire, whatever may be the particular ceramic technique. It served as the base of the crystal glazes in all the work mentioned above. The body fracture is rather dense and gray at a temperature as low as cone 4 to 7. At a somewhat higher temperature, cone 9, this color changes to a light bluish gray and the body now rings clear and is dense. In the commercial kilns, complete maturity comes at cone 7. The body stands however at even higher temperatures, but not without showing the phenomena of an increasingly vesicular structure. This, as is well known, is quite common in bodies that are high in flint. The fusing point is at cone 27. The number of glazes, enamels, colors and engobes, etc., that the body carries without crazing is legion, as are also the decorative possibilities. The natural silver gray color does not act as a disturbing element, but with proper surroundings, and in appropriate setting, the effect

*Stoneware in Germany is not the same as the stoneware in the United States. In Germany they use a blended body as will be seen by description later in this paper.

is extremely distinguished. The fine stoneware is the material which oqers the artist his best field, as it does not detract from the pleasure in the work by too freqeunt failures. The composition of the fine stoneware body used by me for years with the best success is as follows:

45.00	Clay Substance
43.00	Quartz
12.00	Feldspar
100.00	

The clay is obtained by a rather careful washing whereupon the other substances, in finely ground condition, are added and mixed thoroughly. The mass may also be obtained by grinding together the constituents in the ball mill for several hours, the degree of fineness desired dtermining the time. The unwashed crude clay alone can be used to advantage, because the materials which it carries by nature are thoroughly pulverized and hence have no harmful influences, but rather they afford an opportunity to save material that would otherwise have to be added.

The calculation of the body mixture is based upon the rational analysis. The result of the mixtures made is controlled from time to time by chemical analysis.

According to the kind of clay used, this body may be used for every kind of casting work, or it puts difficulties in the way of this process. Because of its great plasticity, which is considerably increased on ageing, it is adapted to all kinds of turning and pressing as well as, or even better than, any white ware body. This is especially true for turning with the free hand (throwing).

The crystal glazes described, may of course, be applied to any other body of sufficient strength, whose maturing temeprature lies within the limits of cones 4 and 10. White ware, however, is practically excluded. The insufficient amount of fluxes in the whiteware body is unable to offer sufficient resistance to the tension caused by the glazes.

It must be said in advance with reference to the burning of crystal glazes that, without exception, they fail of

production in the burning process, continuing for hours in the commercial kilns. Neither the magnificent color effects, nor crystals, nor any other charming phenomena can be realized in this manner. Rather is it necessary that the fusion of crystal glazes take place quite rapidly in a fire that is as neutral as possible, that is, in a fire that is neither predominantly oxidizing nor predominantly reducing. It is also necessary that the cooling take place rapidly. This statement seems to controvert experience. I, too, thought that careful cooling, prolonged as much as possible, would be advantageous to the process of crystal formation, but I changed my opinion when, at a burning, I convinced myself that the perfect and finished crystals covered the vessel even during the last stages of the burning.

Crystals appear rather at a definite stage of the burning, just as Chinese red does. Others again disappear when the temperature is forced still higher. In experiments with new glazes, it is well, therefore, to illuminate the interior of the muffle, by means of a burning splinter from time to time, as the burning progresses, to satisfy one's self of the state of affairs and be guided accordingly.

Dr. Heinecke described an apparatus that is well adapted to such a firing-technique, in Tonindustrie-Zeitung (page 8 of the reprint). It is a so-called high-temperature muffle. This burning apparatus is especially adapted for fine ceramic work. It can be used with safety for every temperature up to about cone 10, and can be regulated. It does not lend itself to the burning of many or of large pieces, but that is not necessary, for reasons discussed above. It does, however, permit the rapid attainment of a comparatively high temperature by a fully developed flame. This makes it possible to obtain magnificent glazes, whose beauty, obtained in the first stage of maturity, is lost by protracted burning in the commercial kilns.

The duration of burning up to cone 10 is approximately but 3½ hours. Such a high temperature could, of course, be attained much sooner by using electric ovens or

coke muffles in connection with a blast, but this would produce no glazes, at least, no serviceable and pretty ones. To secure these, the flame is actually indispensable. A strong draft is required in using this muffle. This is best obtained by means of a high chimney. The regulating can be done by means of a damper, and also by the admission of more or less outside air to the chimney, if the draft is too strong. Finely split pine wood served as fuel, but lignite may also be used or a mixture of lignite and bituminous coal or bituminous coal alone. In this case, however, the more strongly reducing properties of coal-fire must be taken into account.

A detailed description of the Heinecke high-fire muffle is not necessary because of the above reference to the publication in which it may be found with sketches and measurements.

Finally, I desire to call attention to two highly interesting methods for increasing variety in decoration, which at times produce surprising results. There are the commonly known reduction method, and the infiltration method or vapor glazing, which is less known and used and is accompanied with less reduction and which will be described below:

Reduction may be used in several ways. It may be used at a higher or a lower temperature, depending upon the greater or less effects that are desired. But even with higher temperatures, reduction must take place only when the glaze on the surface is already hardened, otherwise the glass coating will readily puff up and be destroyed. At high temperatures, copper oxide is practically completely reduced, and is transformed either into metal or cuprous oxide. The crystal stars are not injured in the least in this process, nor does the gloss of the glaze suffer. The crystals appeared in a far more pronounced character, passing through darker and bright patches and through variously nicely shaded colors. If the crystal glaze contains manganese in addition to copper oxide, then it happens not infrequently that the center of the crystal stars

are colored bright red, while the periphpery remains dark. A very peculiar and charming play of colors is brought about if a little cobalt, uranium, iron, or nickel oxide are present in conjunction with the oxides of copper, manganese, and titanium.

In this reduction at high temperature, some care must be taken that the reduction is not carried too far, or the metallic copper or cuprous oxide will become too pronounced on the surface. It is necessary that they remain covered by the glass, or the well known phenomenon of the gradual fading and disappearing of the fiery luster in the air, especially in sunlight, will readily take place. It is not easy to keep the reduction within the proper bounds, especially when a very strong reducing agent is used at a high temperature. If the reduction takes place at a lower temperature, the process produces beautiful and permanent effects, and does not produce the brilliant though temporary results just noted.

I have carried on the reduction, or have had it carried on in the following manner: After the muffle has cooled off for about three-quarters of an hour, small split splinters of pine wood were thrown in periodically through the peephole, provided for by an opening in the muffle, and this treatment was continued with decreasing numbers of splinters until the temperature had fallen to a red heat. If it is the intention to reduce at low temperature, then the reduction must begin much later, say at 950 C or lower, cone 010, but then it must be carried on energetically and continued until the muffle becomes dark. The trouble with this method is that without a pyrometer, one is frequently deceived concerning the temperature prevailing in the muffle, and for that reason produces a failure.

The following method, however, always produced sure results: Weigh a quantity of pine wood sawdust and spread it on the floor of the muffle, between inserted fire brick supports. On these, place a fire clay plate, so that it will be borne by the supoprts when the sawdust is burned. On this plate, place the objects to be reduced. These may

be selected specially for this purpose, and may be the product of any prvious burning in an oxidizing fire. The muffle is closed and slowly fired. As soon as the walls begin to glow, the products of distillation are developed from the sawdust. The slow firing is continued until the gases ignite of themselves when air enters on opening the peephole, which must be done with caution. Then the fire in the kiln is extinguished at once, and with closed drafts, everything is left to itself. Continued heating would surely result in the puffing up and complete destruction of the glaze layer. According to results, the weight of the reducing agent must be increased or diminished, and the quantity adapted to any particular glaze will soon be found.

What has been said here is by no means to be interpreted as intimating that illuminating gas, petroleum, oil, resin, oxalic acid, carbonic oxide, etc., are not just as well suited to the purpose as pine shavings or pine-wood sawdust, or those other varieties of wood. I merely make mention of the method that was used by me with advantage.

The most charming productions were obtained however by the method of infiltration—a process related to reduction and which possibly has some connection with weak reduction effects, but which never leads to the reduction of copper silicate. The method was worked out from certain scattered statements in literature concerning the possibility of coloring certain crystalline rocks, crystals, gems, etc., with organic matter. This led to the thought that it might be possible to saturate the extremely small spaces and interstitial laminations of the individual crystals, which might be accessible from without, with some organic liquid, and in this manner, perhaps together with slight reduction, secure decorative effects of peculiar kinds. Surprising and successful results were obtained by the following method of procedure:

The object experimented upon, coated with a crystal glaze was placed in a sufficiently wide, cylindrical pot made of soft-burnt clay or fire brick. It was placed in the

center of this pot, and not only imbedded in and surrounded with sawdust firmly tamped, but also covered with a thick layer of sawdust. The pot was then closed with a lid luted on with clay (loam), placed in the muffle and slowly heated. As soon as the walls and floor of the muffle begin to glow, the evolution of the products of distillation from the pot begin, and escape from under the lid. As soon as these ignite because of the air streaming in at the peep-hole (Caution!) the fire on the grates is extinguished immediately, and the kiln left to itself. On cooling, the vase is found to be encased in the finest charcoal, and partly covered by a layer of carbonized tar, which may easily be removed by rubbing with sand or washing with turpentine. The gloss of the glaze has not changed, but the whole appearance of the crystal glaze has. It has become more transparent, as it were, towards the bottom. It seems as if the crystal stars no longer lie in one and the same plane, but rather in several. They have become clearer, more plastic, and because of that more interesting. It seems as if one is no longer dealing with a thin layer of glaze, but rather with a furbished, polished crystalline rock. The most charming thing of all, however, is, that a wonderful play of colors, in the most delicate graduation of shades and merging of one into the other has appeared. This is especially true of those crystal glazes that have, as a background a colored ground glaze, and in which many coloring oxides were used, especially the oxides of cobalt, uranium, nickel and iron, but always in very small quantities. Uranium oxide, especially, which after the vapor process shows a most delicate gold color, now gives to the whole a much more animated appearance by virtue of its delicate shadings. (See glazes 6 and 8, as well as 12, 13 and 14). Color effects are produced by this method such as are impossible by other methods with the aid of fire technique. I hope that many persons who are interested in and enthusiastic over the possibilities of crystalline glazes will find a valuable hint in this communication.

This method has, however, at least one disadvantage.

The walls of the vessel within the bed of sawdust, the latter being not uniformly thick and a poor conductor of heat, will probably not be heated uniformly. The vessels of fine stoneware therefore occasionally came out cracked, while those of coarser material stood the process well. For the former, the process of placing the vessels over a bed of sawdust covered by the firebrick plate, as described above under the reduction process for crystal glazes, was used, but the heating was not carried too far—only to the point of giving off products of distillation. This process proved to be similar to the infiltration method to a certain degree, but the most beautiful and delicate results were always obtained from the vapor treatment in the pot. Even at present, I am engaged in developing this latter method, so that injury to vessels to be treated, which are often of great value, may be reduced to a minimum.

For purpose of comparison, I again give below the three crystal glazes that contain copper oxide as the coloring agent, and which gave the most reliable results. They are give in the order of their gradual development, down to the best results to date.

4	0.396 PbO 0.209 CuO 0.119 Na_2O 0.118 K_2O 0.079 BaO 0.079 CaO	0.079 Al_2O_3	2.137 SiO_2 0.518 TiO_2 0.237 B_2O_3
10	0.412 PbO 0.176 CuO 0.165 CaO 0.165 Na_2O 0.082 K_2O	0.082 Al_2O_3	2.059 SiO_2 0.491 TiO_2 0.165 B_2O_3 0.060 V_2O_5
20	0.333 CuO 0.240 PbO 0.167 CaO 0.113 Na_2O 0.080 K_2O 0.067 MgO	0.187 Al_2O_3 0.047 Fe_2O_3 0.017 Mn_2O_3	2.332 SiO_2 0.403 TiO_2 0.227 B_2O_3 0.001 WO_3

True to my original intention, I refrain from making any theoretic speculations. This is the only advisable

course, since there is not yet sufficient material at hand for such speculations. All preconceived theoretical opinions on the underlying laws of these processes have always been crossed by new facts, which arose quite unexpectedly, and which could not be brought into harmony with them. Theories that do not work out are not only of no good but rather cause confusion. In the following propositions I wish to gather together the results of the work as described in this article, but by no means do I wish to assert that they are of universal validity.

(1) It is not advisable to fritt titanic acid or rutile. This is also true of the metal oxides and other admixtures.

(2) Glazes containing copper and manganese oxide or mixtures of both, give the best results.

(3) Crystals are developed to the best advantage at temperatures between cone 4 and 7.

(4) Small additions of vanadic, molybdic, and tungstic acid promote the development of crystals, but their effect is not the same in all cases. In each individual case, it must be determined which one of the three acids exercise the best influence. Small quantities of iron oxide have likewise frequently a surprisingly favorable effect.

(5) The influence of a ground glaze upon the development of the crystal glaze is but trifling. Frequently it even contributes considerably to the favorable development of the latter.

(6) It is advantageous to use a very easily fusible fritt and to charge it rather heavily with raw metallic oxides, rutile, etc., as well as with those raw substances that are required for a proper glaze formation. The formation of crystals seems to depend not only upon the chemical composition of the glaze, but also on certain external details, as for instance, the solvent power of the fritt, etc.

(7) Fine stoneware is especially well adapted as a base for the production of rutile crystal glazes.

(8) For the production of pretty titanium crystal glazes, a rapid rise of temperature to the maturity of the body is required. Slow cooling does not seem to be neces-

sary, since the requirements for crystal formation, as well as the crystals, are already present, if at all. Rather is it necessary to determine the period of the beginning of crystal formation and to regulate the burning accordingly. Strongly reducing fire gases are to be avoided, but strongly oxidizing ones also act unfavorably.

(9) The effects of reduction are variously manifested according to the temperature prevailing during the reduction. It must never be begun before the glaze on the surface has become hard.

(10) By the process of infiltration or vapor treatment color schemes and effects may be obtained that are hard to duplicate by other processes.

A CHEAP ENAMEL FOR STONEWARE.

BY

R. T. STULL, Urbana, Ill.

The object of this work was to investigate some of the possibilities of producing a cheap enamel, primarily for the improvement of the better grades of stoneware, and secondly, cheap enamels for other purposes at temperatures lower than those required for the stoneware industry. The main object sought for was an enamel which would be whiter and better than the commercial stoneware glaze; something on the order of a tin enamel in appearance, though much cheaper.

No special field was plotted for investigation. The method first adopted for carrying out the work was to make up a series of glazes, then select the most promising one, after firing, for the upper member of the next series, and continuing thus.

The method of preparing and applying each glaze in this work was the same, so as to obtain an accurate comparison of results in so far as mechanical and physical application was concerned. The batch weight of each glaze was calculated from its respective formula, weighed separately, (500 gm.), ground wet for two hours in a small porcelain ball mill, passed through a 100 mesh sieve, placed in a Mason jar, allowed to settle and the water decanted. Sufficient water was then added in order to "set" the glaze at 1.5 B. & L. hydrometer (equal to about 48 to 52 Beaume). Each glaze was then ready for dipping.

Trials were made from ready prepared stoneware clay from Monmouth, Ill. A test showed that the clay when made into slip form readily passed a 60 mesh screen but left quite a residue of dark colored granular particles on the 100 mesh screen.

Trial pieces nested in "Fives" ready for the Sagger.

The trial pieces were made in the form of small "milk" crocks 3″ across the top and 1½″ high. These were made in plaster molds on a jigger and finished outside on a "potter's chum."

The trials were dipped in the bone dry condition, each piece being immersed in the glaze about 2½ seconds. The dipped pieces were then placed on a potter's wheel, the glaze turned off from the rim and shoulder and the pieces nested in "fives" for setting in saggers.

In order to determine the relative fusibility of the glazes, cones were made from each mixture and the bending points or softening temperatures determined by Seger cones and the Le Chatelier pyrometer.

All the glazes in this work were fired in the down-draft open fire kiln of the ceramic department at the University of Illinois. Series I was fired to cone 6 in 12 hours, coke being the fuel used.

For the starting point of this work, a glaze having the following formula* was selected:

$$\text{No. 1, Series I} \quad \left.\begin{matrix} .3\ K_2O \\ .4\ CaO \\ .3\ BaO \end{matrix}\right\} .4\ Al_2O_3 \quad 3.75\ SiO_2$$

This formula produces a clear bright glaze having a range of temperature from cone 4 to cone 8, within which it is a good glaze.

*Sprechsaal; 1905, No. 42.

SERIES I. Formula.							Percentage Batch Weights.						°C.
Glaze	K_2O	CaO	BaO	ZnO	Al_2O_3	SiO_2	Brandywine Felspar	Georgia Kaolin	Whiting	Barium Carbonated	Zinc Oxide	Flint	Temperature at which Glaze Softens.
No. 1	.3	.4	.30	0	.4	3.75	42.09	6.50	10.07	14.89	....	26.45	1200°
No. 2	.3	.4	.20	.10	.4	3.75	43.36	6.70	10.38	10.22	2.10	27.24	1190°
No. 3	.3	.4	.15	.15	.4	3.75	44.02	6.80	10.54	7.78	3.20	27.66	1180°
No. 4	.3	.4	.10	.20	.4	3.75	44.70	6.90	10.70	5.27	4.33	28.10	1150°
No. 5	.3	.4	0	.30	.4	3.75	46.14	7.12	11.04	.....	6.71	28.99	1110°

SERIES II. Formulæ.							Percentage Batch Weights.						°C.
Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	Brandywine Feldspar	Whiting	Boneash	Zinc Oxide	Georgia Kaolin	Flint	Temperature at which Glaze Softens.
No. 5	.3	.4	.3	.4	3.75	0	46.14	11.04	.....	6.71	7.12	28.99	1110°
No. 6	.3	.4	.3	.4	3.75	.03⅓	46.10	8.28	2.84	6.70	7.12	28.96	1160°
No. 7	.3	.4	.3	.4	3.75	.06⅔	46.05	5.51	5.70	6.70	7.11	28.93	1200°
No. 8	.3	.4	.3	.4	3.75	.10	46.01	2.75	8.54	6.69	7.10	28.91	1230°
No. 9	.3	.4	.3	.4	3.75	.13⅓	45.97	.....	11.36	6.69	7.10	28.88	1250°

The first series was made for the purpose of determining the relative fusibility, brilliancy and opacity induced by BaO as against ZnO, by gradual replacement. The formuluæ and batch weights of series I are:

Appearance of Trials.

The softening temperatures expressed in degrees centigrade are given in the column at the right of percentage batch weights above. When taken from the kiln, all five glazes were well matured, and showed no bad defects. After two days' time crazing began to appear in all glazes except No. 5. Crazing was worst in No. 1, gradually decreasing toward No. 5, which was free from crazing.

No. 5 is the most fusible glaze in the series and has the best brilliancy and opacity; opacity not very great.

SERIES II.

No. 5 from series I being the best glaze, was selected for the starting point of Series II, in which the CaO from whiting was gradually replaced by CaO from bone ash, all other members remaining constant. This, of course, increased the acidity by the amount of P_2O_5 brought in with the bone ash.

After series II was made, it was thought that the use of raw bone ash might cause defects such as blistering and curdling, consequently series III was made, keeping the same formulæ as in series II but having the bone ash calcined with flint. This calcine was marked "A."

Calcine A Formula:	Percent Batch Weights:
1. CaO, 1. SiO_2, $\frac{1}{3}$ P_2O_5	Bone Ash 63.19
Combining weight 163⅓.	Flint 36.81

This mix gave a friable mass when burned to cone 6.

SERIES III.

Percentage Batch Weights. °C.

Glaze	Brandywine Feldspar	Whiting	Calcine A	Zinc Oxide	Georgia Kaolin	Flint	Softening Temperature
No. 6A	46.09	8.28	4.50	6.70	7.12	27.31	1160°
No. 7A	46.05	5.51	9.00	6.70	7.11	25.63	1200°
No. 8A	46.01	2.75	13.50	6.69	7.10	23.95	1230°
No. 9A	45.97	....	17.97	6.68	7.10	22.28	1250°

All glazes except No. 5 in series II flaked off after dipping. If the trial pieces were jarred after drying, the glazes shelled off leaving the trials bare. None of the trials in series III showed signs of flaking after dipping.

In order to test the relative effects of raw and calcined bone ash, 3% of dextrine was added to glazes 6, 7, 8 and 9 of series II after which they dipped very nicely, giving no trouble in flaking when dry, but later flaked some during burning.

Glazes from series II and III were placed in saggers and fired to cone 6 in 11 hours.

Appearance of Trials.

There is no appreciable difference in fusibility between those glazes which contained raw bone ash and the corresponding ones in which it had been calcined with flint.

Glazes No. 5, 6 and 7 of series II and 6A and 7A of series III were matured; Nos. 8 and 9, 8A and 9A were dull in appearance due to insufficient temperature to mature them.

Since the members in the two series highest in bone ash were immature, it was decided to make a second firing of series II and III to cone 8. The trials were set and the kiln finished in 14 hours. On opening the kiln, the cones showed evidence of a much higher temperature than cone

8, probably cone 9 at least. All the softer glazes showed evidence of overfiring, showing a sort of "pitted" or egg-shell surface. 8 and 8A, 9 and 9A were nicely matured. No blistering or serious crawling occurred. Nos. 9 and 9A were whitest, whiteness decreasing toward No. 5. Nos. 9 and 9A were crazed in fine meshes, the crazing gradually decreasing toward No. 5.

SERIES IV.

No. 9A is the best as to working qualities and whiteness, though crazed and too refractory for the best development of the stoneware body used. This glaze was selected for the upper members of series IV. The object undertaken was to "soften down" 9A and at the same time overcome the crazing and retain as much of its whiteness as possible.

In order to do this the most promising method seemed to be to introduce B_2O_3 in the form of calcium borate. By replacing part of the SiO_2 with B_2O_3, the softening of the glaze and the overcoming of crazing might be accomplished. The introduction of calcium borate was looked upon as a possibility for retaining the whiteness, since it sometimes produces opalescence in glazes.

In order to save the time and trouble of making a fritt, the naturally occurring mineral "Colemanite" was used. This is the mineral from which our borax and boracic acid is largely obtained. Its formula is $2\,CaO,\ 3\,B_2O_3,\ 5\,H_2O$. Molecular wt.=412. Combining wt. 1. RO=206. According to Dana* colemanite crystallizes in the monoclinic system, usually in short prisms. Cleavable, b-highly perfect; c—distinct. Before the blowpipe; decrepitates, exfoliates, sinters and fuses imperfectly.

Series IV was produced by gradually replacing part SiO_2 in glaze No. 9A, .2 equivalents at a time, by B_2O_3 in the form of colemanite, up to 1.0 equivalent of B_2O_3. By introducing 1.0 B_2O_3 as colemanite, .6⅔ CaO was carried in. This replaced .3 ZnO and .3⅔ CaO from bone ash, giving glaze No. 14 in the table below:

*A Text Book of Mineralogy, pp. 519, 520.

SERIES IV. Formula.								Percentage Batch Weights.						°C.
Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Brandywine Feldspar	Colemanite	Calcine A	Zinc Oxide	Georgia Kaolin	Flint	Softening Temperature
No. 9A	.3	.40	.30	.4	3.75	.133	0	45.97	.....	17.96	6.67	7.10	22.28	1250°
No. 10	.3	.46	.24	.4	3.55	.109	.2	45.60	7.50	14.55	5.30	7.01	20.04	.....
No. 11	.3	.52	.18	.4	3.35	.084	.4	45.21	14.85	11.20	3.95	6.98	17.81	.....
No. 12	.3	.58	.12	.4	3.15	.060	.6	44.85	22.11	7.90	2.60	6.92	15.62	.....
No. 13	.3	.64	.06	.4	2.95	.035	.8	44.52	29.28	4.37	1.31	6.88	13.64	.....
No. 14	.3	.70	0	.4	2.75	.011	1.0	44.15	36.26	1.42	....	6.82	11.35	.....

The trials, and cones made from the glazes for the fusibility test, were set in the kiln in the same manner as in the previous burns. Before a dull red heat was reached, all the cones made from those glazes containing colemanite crumbled to a fine powder on the placque. No. 9A, containing no colemanite, remained standing. Powdered colemanite dehydrates at a very low heat, swelling to nearly twice its original volume without softening, which accounts for the "falling to powder" of the cones made from those glazes in which colemanite was present.

The first intention was to fire the trials to cone 6. From the behavior of the cones it was assumed that the colemanite glazes would crumble from the trials, hence the kiln was finished at cone 8 in order to mature No. 9A.

Appearance of the Trials.

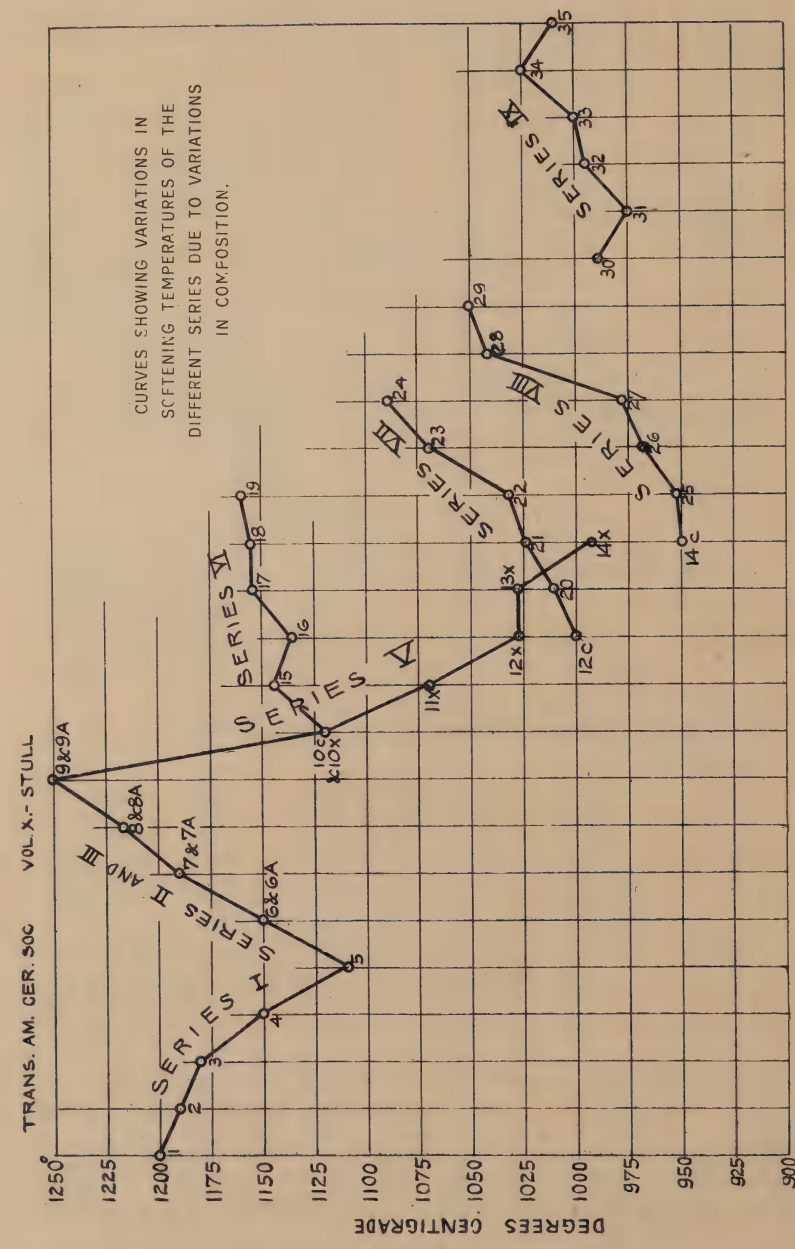
No. 9A softened at 1250°C the same as in the previous burn, going down with cone 6. It was impossible to determine the softening points of the other members of this series since their cones crumbled to powder in the early stage of the burning.

No. 9A matured nicely, is a little whiter than in the previous burn.

Nos. 10, 11, 12, 13 and 14 crumbled off from the outsides of the crocks leaving them bare, and fell to the bottom on the insides, fusing in thick layers. No accurate conclusions could be drawn from these except that they were much more fusible than No. 9A and overfired.

This is as far as the work has been carried. The next step will be to make a series in which the colemanite has been dehydrated after the same formulæ as those in series IV.

According to the composition and low temperature of fusion of colemanite, it is undoubtedly a valuable flux for the introduction of B_2O_3 in an insoluble form. If it can be had in a reasonable state of purity in sufficient quantities, and at a moderate price, a large portion of the trouble


TRANS. AM. CER. SOC VOL. X.- STULL
CURVES SHOWING VARIATIONS IN SOFTENING TEMPERATURES OF THE DIFFERENT SERIES DUE TO VARIATIONS IN COMPOSITION.
DEGREES CENTIGRADE
1250
1225
1200
1175
1150
1125
1100
1075
1050
1025
1000
975
950
925
900
SERIES I
SERIES II AND III
SERIES IV
SERIES V
SERIES VI
SERIES VII
SERIES VIII
1
2
3
4
5
6&6A
7&7A
8&8A
9&9A
10C
10X
11X
12X
12C
13X
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and expense of fritting can be eliminated. It will also be valuable in simplifying the leadless glaze problem, as well as a valuable flux for hardening terra cotta slips for low fire work.

DISCUSSION.

Mr. Purdy: I will ask Mr. Stull two questions. One is as to the calcium phosphate. We known that increased whiteness and opacity of the glaze can be secured by use of bone ash, but can you use it to any great extent without having crawling?

Mr. Stull: I have not experimented extensively in using bone ash for a glaze ingredient, but here used .4 CaO as bone ash and there was no evidence of crawling. Whether more could be used, I do not know. It materially increases the temperature necessary to mature it.

Mr. Purdy: Bone ash, according to my experience, is a very dangerous substance to use in a glaze of that kind. Another question I will ask, in harmony with Prof. Binns' paper; does B_2O_3 tend to increase the opacity of the glaze? Are you getting a whiter glaze with increased content of B_2O_3?

Mr. Stull: I believe it depends on the composition of the glaze whether it imparts whiteness or not. In itself, I do not believe it does. But colemanite is borate of lime, practically insoluble when cold, though it fuses by itself at a low heat, and the theory is advanced that whiteness can be obtained by incorporating calcium borate into the glaze, which precipitates or segregates within the glaze. That is what I intend to follow out. The line of inquiry will be changed from time to time as results from the kiln warrant. I do not believe that B_2O_3 can take the place of Al_2O_3, or that it will act as Al_2O_3 does. In nature, in all the boracic acid minerals, B_2O_3 takes the part of an acid.

Mr. Humphreys: I will ask Mr. Stull what form of whiting he used. I think that is important in comparing with bone ash for temperature. In some recent experi-

ments I found as much as a difference of two cones in the different whitings.

Mr. Stull: I am not prepared to say where it was obtained. I found it in the laboratory there.

Mr. Purdy: The whiting was ordered from the Illinois Supply Co., East St. Louis.

Mr. Mayer: Mr. President, I was not present when all the paper was read, but I heard him mention colemanite. I made some experiments with some colemanite, the analysis of which was:

B_2O_3	54.80
CaO	29.50
H_2O	13.50
Carbonate & Sulphate of Lime and Silica	2.00
	99.80

The experiments were made with a raw glaze of exactly the same composition of the fritted glaze we were using right along. The note I made was, "good glaze, apparently as good, as brilliant as the ordinary glaze, suits colors as well as our regular glaze." It was much better color than our own glaze. I have experimented largely with different forms of colemanite. There is only one discouraging feature and that is we cannot buy it cheaper than borax and boracic acid. Did Mr. Stull ask the price of this colemanite? I found that the trouble. We could get any amount of it and extremely pure, very little impurity in it—white as snow; but they want an unearthly price for it. I did not get mine from the Pacific Coast Borax Co. I got it from a firm that had just found some deposits of extreme purity. The only trouble is the high price the people want for it. In practice they make glazes identically the same. I have not seen any peculiarity about it.

Mr. Binns: I will ask Mr. Mayer if he dehydrated the colemanite?

Mr. Mayer: I just used the colemanite as it comes from the mines.

Mr. Binns: And you did not experience the trouble Mr. Stull had on account of the pulverizing of the glaze?

Mr. Mayer: I never had any such experience, and I used colemanite from three different firms. The last one I experimented with was an extremely pure sample. I never saw that difficulty in any of them. It is extremely hard, very difficult to grind. I broke several mortars before I learned how to break it up.

Mr. Binns: Although not germane to this discussion, Mr. Chairman, I want to speak concerning Mr. Stull's last statement. In mineralogy there is one case of boron as a base, as I said yesterday. Datolite is a silicate of boron and calcium. The claim which I made yesterday was for boron in the presence of silica, which must not be ignored. I granted that boron acted as an acid in the presence of bases.

I am interested in Mr. Stull's optimism when he thinks the difficulty of leadless glazes may be solved by the use of colemanite. I do not think the difficulty of a leadless glaze lies in the expense of fritting, rather in the manipulation of the process. I am interested in the development of the use of bone ash, and there are one or two points which seem to me need more light. My experience has been rather on the line of Mr. Purdy's', that bone ash is dangerous to use. If intended to be used on a large scale, on a large mass of ware, that is where the trouble would come in.

I will ask Mr. Stull in that connection what his experience was in calcining bone ash with flint; to what temperature he took it; what he tried to accomplish, and if he thinks he accomplished his purpose?

Mr. Stull: Answering Mr. Mayer's question, these experiments were carried out on the strength of the new deposit which has been discovered, and I am told that the Pacific Coast Borax Co. have carloads of it. The representative of this company said, in answer to a question, that they could furnish it, but I do not know at what price. I

have not gotten the price yet. As I stated, we will have to investigate the matter of price.

The mineral which Mr. Mayer speaks of as colemanite is not colemanite, but partially dehydrated colemanite. It is of the same composition as colmanite except that it is partially dehydrated. There is a deposit in Oregon of this dehydrated colemanite. That, of course, being partly dehydrated would not decrepitate and would not give the trouble I experienced with colemanite, the trouble of the true mineral colemanite which contains 21.90% H_2O.

Replying to Mr. Binns' inquiry in regard to the use of bone ash, my experience is limited to this case. I had no trouble at all. I made three burns, six, eight and nine, and in no case did I run into blistering. The great difficulty I had with the raw bone ash was that it flaked off badly. It fell off by itself in the drying. The idea of calcining it with flint was that in the manufacture of bone china it is often found necessary to recalcine bone ash to prevent blistering, etc., and I thought it best to recalcine it with a little flint and grind it and use it in that form. There was no special reason except to get a soft mass—not to burn too hard, though it would not harden by itself.

Mr. Binns: I was born and raised on bone china and that is news to me. The calcining of feldspar, without producing any chemical change produces a physical change; but I did not see how the calcining of bone ash could have any effect, as it has already been calcined.

Mr. Stull: I do not know anything about bone china, never saw it made; and as I said, my only experience in the use of bone ash was in this case. Professor Bleininger suggested calcining it for that reason, and I think the German literature has something about the calcining of bone ash as obtained from the dealer, and gives instances where the trouble was overcome by recalcining.

Mr. Mayer: Mr. Stull says the colemanite I got was not colemanite. I am not a mineralogist and do not pretend to know about these things, but I give you the name they call it. They sometimes call it "pandermite" and some-

times colemanite. I cannot tell the difference. I know it had 13.50% water in it. That I will vouch for. I think the man who gave me the sample is as much of a mineralogist as I am, and he sometimes calls it pandermite and sometimes colemanite. But it gave excellent results. The price made it simply out of the question to use.

Mr. Bleininger: The main object of Mr. Stull's experiments is twofold,—one practical and one more theoretical. The practical object is to obtain a cheap stoneware glaze for a certain type of stoneware. The second is to make large and extensive experiments which will tend to show the various opacifying agents. Therefore, he has undertaken the work to show how the various opacifying agents behave and produce workable glazes.

Mr. Binns: If Mr. Mayer's glazing was done on biscuit ware and Mr. Stull's on green ware, it may be possible that the combined water in the clay may have caused decrepitation.

Mr. Stull: It occurred before the kiln was red enough to see the cone. May I ask Mr. Mayer what percent of water was in the dehydrated colemanite he used?

Mr. Mayer: The composition of the glaze in which I used this colemanite was:

Feldspar	271.7
White Lead	105.0
Florida Clay	59.2
Colmanite	150.0
Whiting	44.8
Flint	139.6

Mr. Stull: In pure colmanite there is 21.90% H_2O. I will ask Mr. Mayer what was the percent of water in his variety?

Mr. Mayer: 13.50 of water.

Mr. Stull: It was probably half way between hydrated and dehydrated colmanite.

*CONTINUATION OF THE WORK.

The next step decided upon was to make up several glazes representing five different series, determine their softening temperatures in the form of cones, group these glazes according to their softening temperatures and fire them accordingly.

Since the glazes in series IV in which raw colemanite was used powdered from the trial pieces, series V was made according to the respective formulæ in series IV, the only difference being that the colemanite was dehydrated.

SERIES VI, VII AND VIII.

These series were constructed for the uprpose of determining the effect of increasing Al_2O_3 and P_2O_3 by the use of aluminum phosphate in the presence of calcined bone ash and B_2O_3.

Since the sample of colemanite at hand was exhausted in making series V, and since letters to two borax companies brought replies that they had no colemanite for sale as it was all absorbed by their plants in the refining of borax and boracic acid, it was decided to make a fritt after the dehydrated colemanite formula for use in the three following series. This was designated "Fritt B."

Fritt B.	Batch Weights:
Formula	Whiting 50
$2\,CaO,\ 3\,B_2O_3$	Boracic Acid 93

A preliminary test in the Pelton electric furnace shows that this mixture swells at 700°C to a porous sponge-like mass and melts to a clear, water-like fluid at 950°C. An attempt to make a drop fritt of this mixture had to be abandoned on accoutn of its great fluidity and corrosive action. It soaked through the fire clay crucible, draining

*This installment represents the work which has been done on "A Cheap Enamel for Stoneware," between the last convention and the date of publication.

SERIES V.

Formulæ.

Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	B_2O_3
No. 10X	.3	.46	.24	.4	3.55	.109	.2
No. 11X	.3	.52	.18	.4	3.35	.084	.4
No. 12X	.3	.58	.12	.4	3.15	.060	.6
No. 13X	.3	.64	.06	.4	2.95	.035	.8
No. 14X	.3	.70	0	.4	2.75	.011	1.0

Percentage Batch Weights.

Brandywine Feldspar	Calcine A	Dehydrated Colemanite	Zinc Oxide	Georgia Kaolin	Flint	°C. Softening Temperature
46.35	14.18	5.95	5.39	7.16	20.35	1120°
46.73	11.56	12.01	4.08	7.22	18.40	1077°
47.12	8.29	18.16	2.74	7.27	16.42	1027°
47.37	4.93	24.66	1.38	7.32	14.34	1027°
47.93	1.56	30.78	....	7.40	12.33	992°

SERIES VI.

Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	B_2O_3
No. 10C	.3	.46	.24	.40	3.55	.109	.2
No. 15	.3	.46	.24	.43	3.55	.139	.2
No. 16	.3	.46	.24	.46	3.55	.169	.2
No. 17	.3	.46	.24	.49	3.55	.199	.2
No. 18	.3	.46	.24	.52	3.55	.229	.2
No. 19	.3	.46	.24	.55	3.55	.259	.2

Fritt C	Brandywine Feldspar	Calcine A	Zinc Oxide	Georgia Kaolin	Flint	Aluminum Phosphate	Softening Temperature
15.40	37.08	14.50	5.39	7.16	20.47	....	1120°
15.09	36.34	14.22	5.29	7.01	20.06	1.99	1145°
14.80	35.63	13.94	5.18	6.88	19.67	3.90	1137°
14.52	34.95	13.66	5.08	6.75	19.30	5.74	1155°
14.24	34.30	13.41	4.99	6.62	18.93	7.51	1156°
13.98	33.66	13.16	4.90	6.50	18.58	9.92	1161°

SERIES VII. Formulæ.								Percentage Batch Weights.							°C.
Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Fritt C	Brandywine Feldspar	Calcine A	Zinc Oxide	Georgia Kaolin	Flint	Aluminum Phospate	Softening Temperature
No. 12C	.3	.58	.12	.40	3.15	.06	.6	46.99	18.86	7.37	2.74	7.28	16.76	....	1000°
No. 20	.3	.58	.12	.43	3.15	.09	.6	46.04	18.48	7.22	2.69	7.13	16.42	2.02	1010°
No. 21	.3	.58	.12	.43	3.15	.12	.6	45.13	18.11	7.08	2.63	6.99	16.09	3.97	1025°
No. 22	.3	.58	.12	.49	3.15	.15	.6	44.25	17.76	6.94	2.58	6.85	15.78	5.84	1033°
No. 23	.3	.58	.12	.52	3.15	.18	.6	43.41	17.42	6.81	2.53	6.72	15.48	7.63	1070°
No. 24	.3	.58	.12	.55	3.15	.21	.6	42.59	17.09	6.68	2.49	6.60	15.19	9.36	1090°

SERIES VIII. Formulæ.							Percentage Batch Weights.				°C.
Glaze	K_2O	CaO	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Fritt C	Georgia Kaolin	Flint	Aluminum Phosphate	Softening Temperature
No. 14C	.3	.7	.40	2.75	.011	1.0	79.68	7.41	12.91	....	950°
No. 25	.3	.7	.43	2.75	.041	1.0	78.04	7.25	12.65	2.06	952°
No. 26	.3	.7	.46	2.75	.071	1.0	76.46	7.11	12.40	4.03	967°
No. 27	.3	.7	.49	2.75	.101	1.0	74.95	6.97	12.15	5.93	980°
No. 28	.3	.7	.52	2.75	.131	1.0	73.50	6.84	11.91	7.75	1040°
No. 29	.3	.7	.55	2.75	.161	1.0	72.10	6.70	11.69	9.51	1050°

out at the bottom like water through a sponge, and in a short time dissolved the bottom from the crucible completely. In order to increase viscosity and reduce corrosive action, "fritt C" was constructed having the formula:

FRITT C.

$$\left.\begin{matrix}.3\ K_2O \\ .7\ CaO\end{matrix}\right\} .3\ Al_2O_3 \left\{\begin{matrix}1.8\ SiO_2 \\ 1.0\ B_2O_3 \\ .011\ P_2O_5\end{matrix}\right.$$

Combining weight=277.6

BATCH WEIGHTS.	
Brandywine Feldspar	46.26
Whiting	18.46
Flaky Boracic Acid	34.33
Bone Ash	.95

This mixture gave a very satisfactory drop fritt, very white and translucent. This fritt was used in making the three following series:

SERIES IX.

In this series the RO and acid were kept constant in order to note the effect of increasing the Al_2O_3 by using calcined Georgia kaolin. The glaze selected for the first member in this series has the formula:

$$\text{No. 30} \quad \left.\begin{matrix}.2\ K_2O \\ 2\ ZnO \\ .6\ CaO\end{matrix}\right\} .4\ Al_2O_3 \left\{\begin{matrix}2.5\ SiO_2 \\ .2\ P_2O_5 \\ .8\ B_2O_3\end{matrix}\right.$$

A trial fritt marked "Fritt D" composed of bone ash, whiting and boracic acid was tested. Its formula and batch weights are:

FRITT D.

Formula.		Batch Weights.	
1. CaO	$\left\{\begin{matrix}.25\ P_2O_5 \\ 1.33\ 1\text{-}3\ B_2O_3\end{matrix}\right.$	Bone Ash	28.94
		Whiting	9.34
		Flaky Boracic Acid	61.72

A portion of this mix when tested in the Pelton furnace softened at 760°C and fused to a thick viscous paste at 1165°C. On testing for solubility in hot water, it was found that the B_2O_3 dissolved readily, leaving a fine white paste of bone ash and calcium borate. This shows the stability of bone ash in the presence of B_2O_3, since no

SERIES IX. Formulæ.								Percentage Batch Weights.						°C.
Glaze	K_2O	CaO	ZnO	Al_2O_3	SiO_2	P_2O_5	B_2O_3	Fritt E	Calcine A	Zinc Oxide	Georgia Kaolin	Calcined Georgia Kaolin	Flint	Softening Temperature
No. 30	.2	.6	.2	.40	2.5	.2	.8	63.85	7.05	2.33	7.43	6.39	12.95	991°
No. 31	.2	.6	.2	.43	2.5	.2	.8	63.29	6.99	2.31	7.36	8.24	11.81	976°
No. 32	.2	.6	.2	.46	2.5	.2	.8	62.74	6.93	2.29	7.30	10.05	10.69	996°
No. 33	.2	.6	.2	.49	2.5	.2	.8	62.20	6.87	2.27	7.24	11.83	9.59	1001°
No. 34	.2	.6	.2	.52	2.5	.2	.8	61.67	6.82	2.25	7.17	13.58	8.51	1026°
No. 35	.2	.6	.2	.55	2.5	.2	.8	61.15	6.75	2.23	7.11	15.31	7.45	1011°

chemical arrangement took place, except the formation of calcium borate with the free CaO from whiting.

On account of its solubility, fritt D could not be used. Instead, fritt E was made.

FRITT E.

Formula.

$$\left.\begin{matrix} .26\ 2\text{-}3\ K_2O \\ .60\ \ CaO \\ .13\ 1\text{-}3\ ZnO \end{matrix}\right\} .26\ 2\text{-}3\ Al_2O_3 \left\{\begin{matrix} 1.6\ SiO_2 \\ .2\ P_2O_5 \\ 1.05\ 2\text{-}3\ B_2O_3 \end{matrix}\right.$$

Cmbining weight=295.733

Batch Weights.

Brandywine Feldspar	42.01
Bone Ash	17.53
Zinc Oxide	3.05
Flaky Boracic Acid	37.41

This mixture makes a beautiful drop fritt; white and opaque, resembling a tin fritt in appearance, and is practically insoluble.

The softening temperatures of all the glazes in series V, VI, VII, VIII and IX were determined by the Le Chatelier pyrometer in the Pelton furnace, the softening points of each series being determined separately. These glazes were then arranged according to their bending temperatures for burning, No. 14c being softest and No. 19 the most refractory. As arranged in the table, all glazes softening between 950°C and 1027°C were fired at cones 03 and 01. Those softening between 1027°C and 1120°C were burned at cone 2, while those bending between 1033°C and 1161°C were fired at cones 4 and 6.

Length of Time of Burning.

Cone 03 was made in 9 hours.
Cone 01 was made in 11 hours.
Cone 2 was made in 18 hours.
Cone 4 was made in 17 hours.
Cone 6 was made in 19 hours.
Coke being used as fuel.

Glaze	°C	
No. 14c	950	
No. 25	952	
No. 26	967	
No. 31	976	
No. 27	980	
No. 30	991	
No. 14X	992	
No. 32	996	Fired at Cones 03 & 01
No. 12c	1000	
No. 33	1001	
No. 20	1010	
No. 35	1011	
No. 21	1025	
No. 34	1026	
No. 12X	1027	
No. 13X	1027	
No. 22	1033	
No. 28	1040	
No. 29	1050	Fired at Cone 2
No. 23	1070	
No. 11X	1077	
No. 24	1090	
No. 10c	1120	Fired at Cones 4 & 6
No. 10X	1120	
No. 16	1137	
No. 17	1153	
No. 15	1145	
No. 18	1155	
No. 19	1161	

In each case after firing was finished, the fire was drawn, the fire box door and damper left open and the kiln allowed to cool quickly.

APPEARANCE OF THE TRIALS.

Series V.

No. 10X. Cone 2: White, smooth, no beading; underfired.

Cone 4—Quite white and opaque, slightly beaded, crazed some.

Cone 6—Opalescent, blisters where thick, crazed. No beading.

No. 11X. Cone 2: Opalescent, crazed, otherwise a good glaze.

Cone 4—A good clear bright glaze. Opalescent where thick, no crazing.

Cone 6—Appearance same as at cone 4 except runs more.

No. 12X. Cone 03: Glaze somewhat immature, smooth.

Cone 01—Bright and opalescent, slightly beads, crazed.

Cone 2—Bright, less opalescent, smooth, no crazing.

No. 13X. Cone 03: Underfired, matt.

Cone 01—Bright, opalescent, beads a little, crazes.

Cone 2—Bright, opalescent, beads a little, no crazing.

No. 14X. Cone 03: Opalescent, bright, crazed some, no beading.

Cone 01—Clear, bright, a few craze marks, no beading.

Series VI.

In both the cone 4 and 6 burns there is a gradual gradation in this series from 10C to 19. All are whiter in the cone 4 burn than in the cone 6 burn. 10C is opalescent, blisters, crawls very slightly, has no crazing. Whiteness, opacity, crawling and crazing increase and blistering decreases from 10C to 19. No. 19 is as white as a tin enamel, though some beaded and crazed.

Series VII.

No. 12C. Cone 03: White, opalescent, tendency to bead, crazed.

Cone 01—Bright, opalescent. Beads some, crazes some.

No. 20. Cone 03: White, opaque, crawls some, blisters some, crazed a little.

Cone 01—Translucent, crawls less, blisters some, crazes less.

No. 21. Cone 03: White, opaque, beaded badly, crazes badly.

Cone 01—White, opaque, beads, crazes, no blistering.

No. 22. Cone 2: White, opaque, beaded, crazed and blistered.

Cone 4—Blisters, no crazing or beading; translucent.

Cone 6—Opalescent, blisters, no beading, no crazing.

No. 23. Cone 2: Blisters slightly, beads and crazes.

Cone 4—Blisters slightly, white, no crazing; beads some.

Cone 6—Opalescent, blisters, no crazing or beading.

No. 24. Cone 2: Badly blistered, slight beading, badly crazed.

Cone 4—Whitest glaze of series. Blisters, no crazing or beading.

Cone 6—Appearance same as in cone 4 burn.

Series VIII.

No. 14C. Cone 03: Opalescent, crazes, otherwise good.

Cone 01—Same as the cone 03 burn.

No. 25. Cone 03: Translucent, crazes, otherwise good.

Cone 01—Opalescent, smooth, bright and crazed.

No. 26. Cone 03: Translucent, whiter than 25, blisters, crazes.

Cone 01—Opalescent, smooth, bright and crazed. Slight beading.

No. 27. Cone 03: Translucent, whiter than 26, crazes, no beading.

Cone 01—Translucent, crazed and beaded.

No. 28. Cone 2: White, opaque, beaded some, crazed, no blistering.

Cone 4—Blistered, crazed, no beading.

Cone 6—Opalescent, blistered, no crazing or beading.

No. 29. Cone 2: White, opaque, beaded, blistered some, crazed.

Cone 4—Blistered badly, crazed, no beading.

Cone 6—Blistered, translucent, no crazing or beading.

Series IX.

Cone 03—This series has given the best results so far. All are white, opaque, though crazed. No. 30 quite badly crazing decreases toward No. 35 which has only three or four craze marks. There is very little difference in this series in whiteness, opacity and brilliancy. The glazes, however, are not at their best, a little higher temperature would improve them. None are blistered. There is a very slight tendency to crawl in No. 30 which appears less in 35.

Cone 01—All the members of the series are beautiful opaque glossy enamels. The appearance is a light ivory in color and texture. No evidence of blistering. No. 30 is crazed slightly; crazing decreases toward 35. Nos. 34 and 35 are not crazed though the body is very soft. Trials were also taken from the kiln quite hot. There is a very slight

tendency in all members to crawl a little in one or two small spots on the outside rim near the shoulder. The insides of the crocks are smooth and practically flawless, aside from those members (Nos. 30, 31, 32, and 33) which crazed. Brilliancy and opacity equal to a good tin enamel, color very nearly as good. An interesting point noticed both in the cone 03 and 01 burns is that the tendency to crawl in No. 35 containing .55 Al_2O_3 is less than in No. 30 containing .40 Al_2O_3, all other members in both remaining constant. The crawling tendency, however, is no greater than that of many good stoneware glazes and tin enamels in commercial use in which raw borax is used to overcome that trouble. Therefore, the enamels of Series IX are very promising, since they contain no raw borax or other soluble salts.

CONCLUSIONS.

Series I.

In this series ZnO causes greater fusibility than BaO. Replacement of BaO by ZnO reduces crazing, increases brilliancy and opacity.

Series II and III.

The use of bone ash direct causes flaking of the glaze after dipping. Flaking is overcome by calcining the bone ash with flint.

Replacement of CaO from whiting by CaO from bone ash increases refractoriness materially and induces crazing.

.13⅓ P_2O_5 introduced as bone ash with .3 ZnO and .4 Al_2O_3 caused no beading and materially increased whiteness.

Series IV and V.

The use of raw colemanite* in glazes causes "powdering" before a dull red heat is reached. Powdering is overcome by using dehydrated colemanite.

Replacement of bone ash, ZnO and SiO_2 by dehydrated colemanite, materially decreases the temperature of fusion, decreases opacity and increases brilliancy.

The opacifying effect of colemanite is very small, producing at best only a small degree of opalescence.

Series VI, VII and VIII.

It is difficult to determine the action of aluminum phosphate in these three series. Increasing Al_2O_3 and P_2O_5 by aluminum phosphate increases the temperature of fusion a little, increases whiteness and opacity.

The blistering which occurs has the appearance of being what "single fire" enamel brick men call "steamed glazes." Opacity, whiteness, blistering, beading and crazing generally seem to be lessened by increase in temperature of firing, though not borne out in all cases. None of the glazes containing aluminum phosphate are good enough for commercial use. It is probable that more consistent results would have been obtained if the aluminum phosphate had been calcined or fritted.

Series IX.

This series shows that good glossy enamels are possible as low as cone 01 with:

$$\left.\begin{matrix} .2\ ZnO \\ .6\ CaO \\ .2\ K_2O \end{matrix}\right\} .40 \text{ to } .55\ Al_2O_3 \left\{\begin{matrix} 2.5\ SiO_2 \\ .2\ P_2O_5 \\ .8\ B_2O_3 \end{matrix}\right.$$

*A distinction should be made between the three most general forms of calcium borate, viz., colemanite, priceite, and pandermite, which have different physical properties such as hardness, specific gravity, action before the blow pipe, etc., as well as differences in their respective chemical analyses. However, both priceite and pandermite are classed as "varieties" under colemanite by mineralogists.

in which bone ash has been calcined or fritted and in which the excess above .3 Al_2O_3 is added as calcined clay.

Experiments with bone ash as an opacifier in glazes are not new, yet the author fails to find any work in ceramic literature pertaining to its use purely as a glaze ingredient aside from its uses in glass and bone china. The question has been raised that bone ash is dangerous to use in glazes on account of its liability to cause beading.

It is a well known fact that an excess of the opacifiers, alumina, tin oxide, zinc oxide and bone ash causes beading. The observations of the writer lead him to believe that bone ash has no greater tendency to cause beading than ZnO, SnO_2 or Al_2O_3. If we attempt to add bone ash to a glaze of the Bristol type, which is already loaded up with an opacifier, bringing it close to the danger point of beading, then of course beading will occur.

This concludes the work to date. The next step will be to test the members of series IX for range of temperature to determine whether they are suitable for commercial use. If so, then the best one of the series will be selected for the starting point of series X, in which the B_2O_3 is to be gradually replaced by SiO_2 in an endeavor to produce suitable "tinless' enamels for higher temperatures.

EFFECT OF FINE GRINDING ON THE PROPERTIES OF PORTLAND CEMENT.

BY

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It is coming to be known through recent scientific investigations that the degree of fineness to which Portland cement clinker is ground has an important influence on the qualities of the resulting cement. Results of investigations along this line have been recently published by Dr. W. Michaelis, Jr.,* S. B. Newberry,† H. S. Spackman and R. W. Lesley, American Association of Portland Cement Manufacturers.

There is a more or less general agreement among those who have entered into the matter that only the most finely divided particles are hydraulically active, within a reasonable length of time, when the cement is mixed with water. That is, only the finest flour possesses hydraulicity, the remainder being inert, like so much sand, so far as its immediate effect on the working qualities of the cement is concerned.

No one seems ready as yet to announce definitely just where the boundary line lies between those particles of cement that are inert and those that are active. The fact that commercial cements have a range in size of particle from 100 mesh down to impalpability renders the determination of the actual sizes a matter not only of delicacy, but of extreme difficulty even with the microscope.

Standard specifications require that not more than 8 per cent remain on the No. 100, and that over 75 per cent must pass the No. 200 sieve. This means that over 75 per

*Journal Western Society of Engineers, Vol. XIII, No. 4, Aug., 1907, p. 455.

†Cement World, Jan., 1907.

cent of commercial cement must consist of grains whose individual diameters range below .0026 of an inch. Dr. Michaelis suggests that only particles of 800 mesh size are cement proper. 800 mesh particles run in diameter from 1-1600 of an inch (.0000625) down, sizes scarcely appreciable when numerically expressed.

In contemplating the above facts, the question arises as to what changes in the nature of Portland cement and its valuable properties pulverization to a greater degree of fineness will bring about. Suppose we reduce it so that the maximum particle will pass the 200, then the 300, 400 mesh and so on. This will mean not only that the upper limit of size is successively lower, but there will also be produced an increasing quantity of the excessively fine cement flour, which is to be regarded as the hydraulically active part. A series of standard tests of such samples would, no doubt, afford results of much scientific interest besides practical value.

To obtain preliminary data to be used as a basis for laying out further experiments, the tests described below were carried out.

A sack sample of a standard brand of Portland cement was purchased in the market. A portion of this was placed in a ball mill and ground for two hours. A second portion was ground for five hours; a third portion for nine hours; and a fourth, fourteen hours. Each of the resulting cements, along with the market product itself, was subjected to the standard tests for cement of the American Society for Testing Materials.

The following table shows the results of the fineness tests. Observance of each column vertically will emphasize the increasing degree of fineness.

TABLE I.

Fineness Tests of Reground Cement.

SAMPLE	Retained on 100 mesh	Passing 100 retained on 200 mesh	Passing 200 mesh
Market	3.45	20.80	75.75
After 2 hours grinding	0.27	11.19	88.54
After 5 hours grinding	0.15	8.75	91.10
After 9 hours grinding	0.02	3.20	96.78
After 14 hours grinding	0.00	1.22	98.78

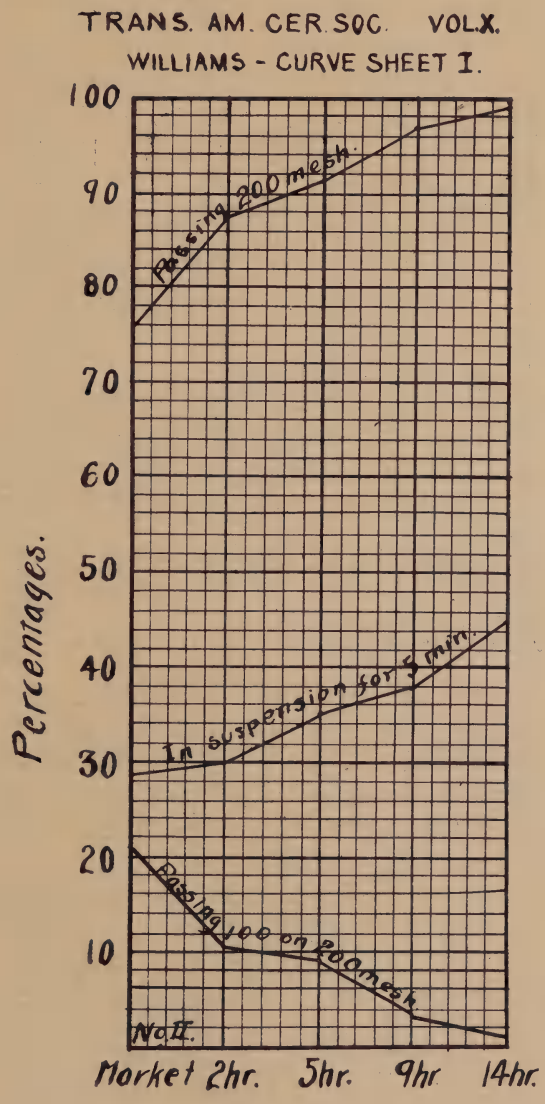
Portions of the cement passing the 200 mesh sieve were further separated into a series of sizes by the settling process, using dry kerosene as the liquid. Settling periods of 30 seconds, 1 minute and 5 minutes, were used. The figures given in the table are percentages, the totals in this compilation being the amounts passing the 200 mesh shown in the table above.

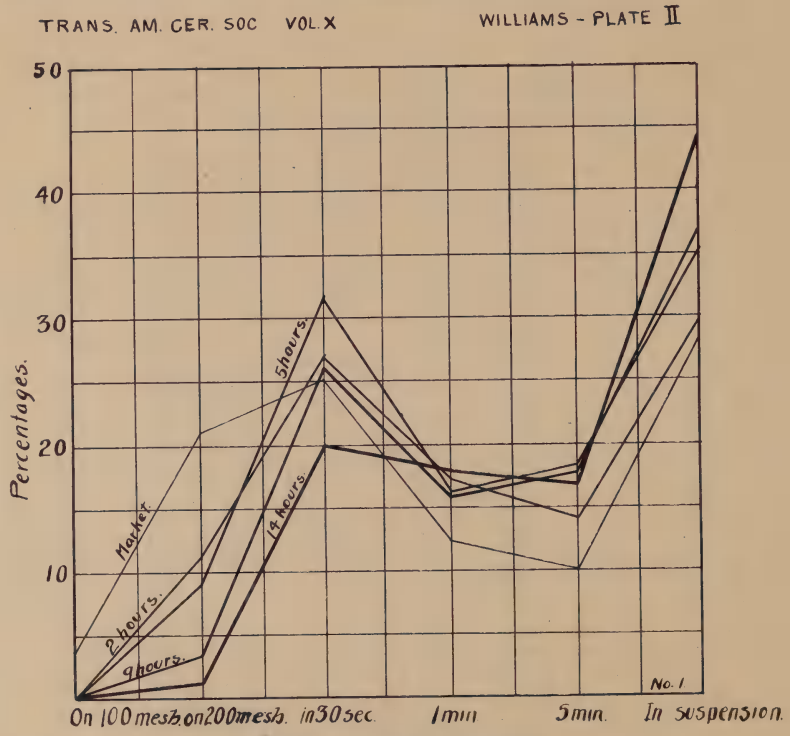
TABLE II.

Fineness Tests of Reground Cement Passing 200 Mesh Sieve.

SAMPLE	Settling from suspension in Kerosene in			In suspension in Kerosene after 5 mins.	TOTAL
	30 secs.	1 min.	5 mins.		
Market	25.43	12.08	9.71	28.53	75.75%
2-hour	27.39	17.42	13.77	29.96	88.54%
5-hour	31.50	16.28	18.17	35.15	91.10%
9-hour	25.93	15.54	17.63	37.68	96.78%
14-hour	19.91	17.21	16.56	45.10	98.78%

The curves, sheets I and II, depict the total composition of each of the samples and emphasize the increase in fineness with successively longer periods of grinding.


TRANS. AM. CER. SOC. VOL X.
WILLIAMS - CURVE SHEET I.
100
90
80
70
60
50
40
30
20
10
Percentages.
Passing 200 mesh.
In suspension for 5 min.
Passing 100 on 200 mesh.
No II.
Market 2hr. 5hr. 9hr 14hr.



TIME OF SETTING.

The smalll samples obtained in the settling analyses were treated with water and their setting properties observed. The time of the initial and final sets was estimated by the needle test. Results are shown in table III.

TABLE III.

Setting Properties of the Different Grades of Cements Obtained in the Settling Analysis.

SAMPLE	Initial set minutes	Final set minutes	Per cent of water
30 seconds	12	30	26
1 minute	7	18	29-30
5 minutes	4	12	33-34
Suspended	2	9	40

The reground cements as they came from the ball mill gave the following results:

TABLE IV.

SAMPLE	Initial set	Final set
Market	45 minutes	3 hours
2-hour	40 minutes	2 hours and 30 minutes
5-hour	30 minutes	2 hours and 15 minutes
9-hour	17 minutes	1 hour and 5 minutes
14-hour	5 minutes	17 minutes

TENSILE STRENGTH.

The strength of briquettes made from the unground commercial cement is given in Table V. The briquettes in all instances were 24 hours in moist air and under water for the remainder of the time. The proper consistency required 23 per cent of water with the neat cement and 9.8% in the 1:3 mixture.

TABLE V.

Tensile Tests Market Cement.

Neat Cement, Lbs. per sq. in. at the end of			1 cement: 3 sand Lbs. per sq. in. at the end of		REMARKS
24 hours	7 days	28 days	7 days	28 days	
					SOUNDNESS.
132	605	810	158	237	
130	595	650	152	208	Passed O. K. in Air
156	545	613	153	187	No sign of defect in water.
155	565	615	167	255	Accelerated:
142	550	610	178	254	No sign of defect
120	515	673	168	252	Pat losened from glass
130	515	645	180	250	Specific Gravity=3.14
128	583	675	158	280	
134	570	662	188	...	
132	510	625	177	262	

TABLE VI.

Tensile Tests, Cement Reground for 2 hours.

Neat Cement, Lbs. per sq. in. at the end of			1 cement: 3 sand Lbs. per sq. in. at the end of		REMARKS
24 hours	7 days	28 days	7 days	28 days	
315	545	635	250	290	Neat cement, 24 per cent water.
322	585	627	280	260	1 cement: 3 sand, 10 per cent water.
327	595	636	200	280	SOUNDNESS.
295	500	515 faulty	200	230	In air, passed O. K.
345	515	585	225	255	In water, passed O. K.
310	495	652	216	308	Accelerated:
340	488	600	207	350	Passed O. K.
338	520	630	200	344	Pat remained on glass.
352	550	600	210	290	Specific Gravity=3.13
335	530	607	245	337	

TABLE VII.

Tensile Tests, Cement Reground for 5 Hours.

Neat Cement, Lbs. per sq. in. at the end of			1 Cement: 3 sand Lbs. per sp. in. at the end of		REMARKS
24 hours	7 days	28 days	7 days	28 days	
353	566	600	270	395	Neat cement + 25 per cent of water.
345	540	645	247	375	1 cement: 3 sand + 10.2 per cent water.
351	600	670	232	368	SOUNDNESS.
325	622	632	237	385	In air, slight shrinkage,
348	540	680	230	335	cracks at edge of pat.
360	570	660	255	350	Short expansion
366	540	605	247	300	cracks, very small and
340	600	600	233	320	few.
340	570	586	243	357	In water, passed O. K.
360	535	635	236	320	Accelerated:
					Passed O. K.
					Specific Gravity=3.14

TABLE VIII. Tensile Tests, Cement Reground for 9 Hours.

Neat Cement, Lbs. per sq. in. at the end of			1 Cement: 3 sand Lbs. per sq. in. at the end of		REMARKS
24 hours	7 days	28 days	7 days	28 days	
310	507	560	277	375	Neat cement + 25 per cent water.
330	540	615	265	373	1 cement: 3 sand + 10.2 per cent water.
322	542	570	250	366	In air, a few small shrinkage and expansion cracks at edge of pat.
305	550	595	243	320	
315	585	650	270	335	
295	580	660	298	330	
300	470	700	278	345	
320	570	617	268	325	In water, passed O. K.
310	490	662	230	355	Accelerated:
309	495	680	298	320	Passed O. K.
					Specific Gravity=3.13

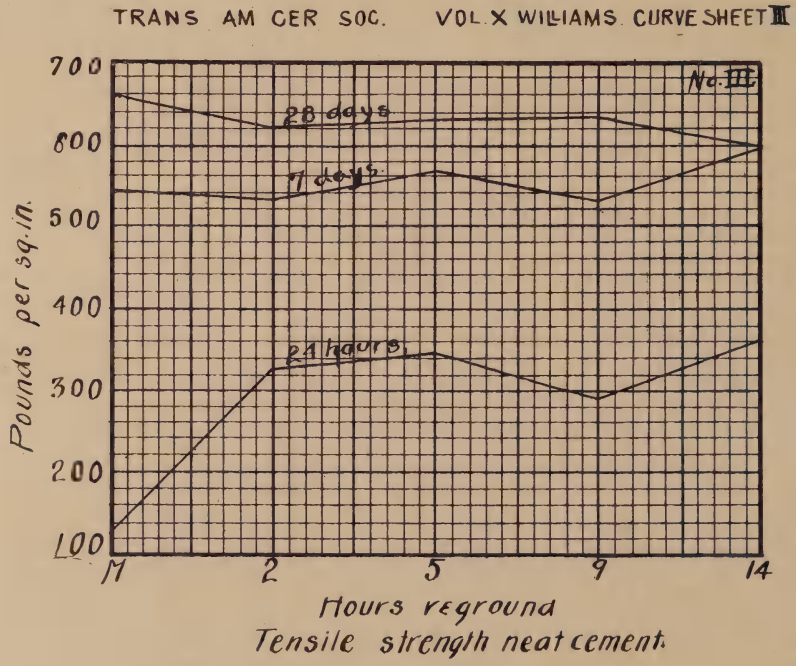
TABLE IX. Tensile Tests, Cement Reground for 14 Hours.

Neat Cement, Lbs. per sq. in. at the end of			1 Cement: 3 sand Lbs. per sq. in. at the end of		REMARKS
24 hours	7 days	28 days	7 days	28 days	
350	510	580	305	397	Neat cement + 25 per cent water.
370	565	538	295	370	1 cement: 3 sand + 10.2 per cent water.
365	545	575	275	356	SOUNDNESS.
385	552	580	265	390	In air, a few small shrinkage and expansion cracks at edge of pat.
370	510	610	286	345	
368	525	615	282	430	
355	515	600	282	388	
376	555	615	290	350	
346	625	635	276	375	In water, passed O. K.
260	575	640	275	405	Accelerated:
faulty					Passed O. K.
					Specific Gravity=3.13

TABLE X. Summary of Tensile Tests Reground Cement.

SAMPLE	Neat Cement, Lbs. per sp. in. at the end of			1 Cement: 3 sand Lbs. per sq. in at the end of	
	24 hours	7 days	28 days	7 days	28 days
Market	135.9	555.3	657.8	167.9	242.7
2 hours	327.9	532.3	619.0	223.3	294.4
5 hours	348.8	568.3	631.3	243.0	350.5
9 hours	291.6	532.9	630.9	257.7	344.4
14 hours	365.0	596.7	598.8	283.1	380.6

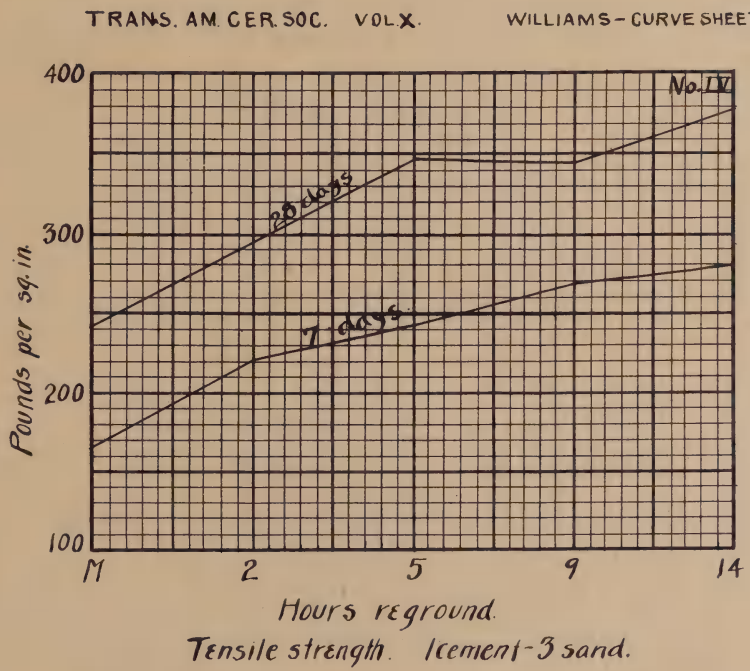
On sheets Nos. III and IV are shown graphically the effects of the degree of fineness on the tensile strength of the neat cement and of the 1:3 mixture respectively. On sheet III it is to be noted that a much different curve is given at the end of 24 hours than at the end of longer periods. The increase in strength is the more decided at the end of one day, the finer the cement. The longer the



setting period, however, the less pronounced this appears to be, and the 28 day curve shows an actual decrease in strength with increasing fineness.

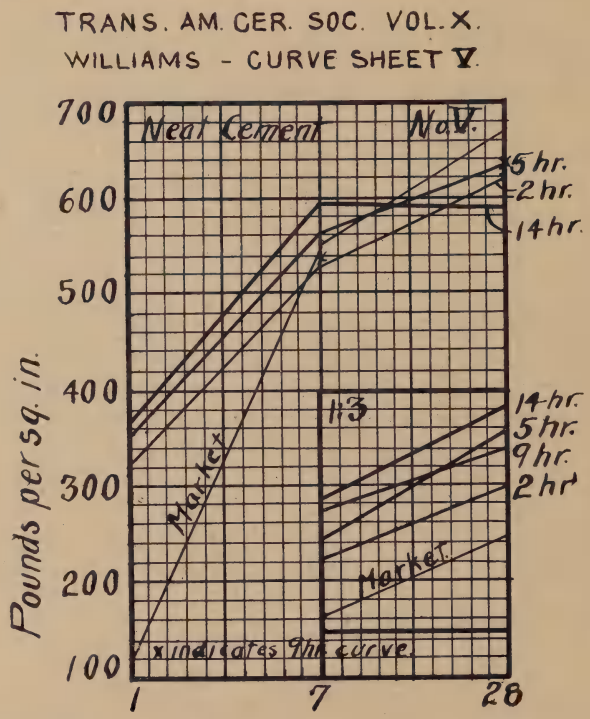
The 1:3 curves show uniform and fairly rapid rise in strength as the period of grinding increases. It is to be expected that whatever effects fine grinding may have on the strength or bonding power of the cement would become most evident when it is used with an aggregate. The neat cement, therefore, appears to reach a high strength quickly.

and increasing its fineness to any great extent not only does not add materially to its strength, but may even lessen it as shown by the 28 day curve (No. III). This may possibly be accounted for by the fact that in the market cement many of the larger particles which are not hydraulic because of their size, serve simply as so much sand or aggregate, which the active part, or the cement



flour, binds together. On regrinding, an increasing quantity of these inert particles is reduced to such a fineness that they become active and the filler or aggregate is decreased by just this amount. The extreme condition would, of course, be realized should the clinker be reduced entirely to the degree of impalpability such that every particle would become immediately hydraulically active. In this instanec the setting reaction would be continuous

throughout the mass of the cement, every particle entering to build a homogeneous solid. There would, literally, be no aggregate and the setting process would be one of mass crystallization or (as regarded by some) colloid formation, as contrasted with the interrupted and insterstitial intergrowth in a less finely ground cement or in a mortar mixture.



The effect on the bonding power of the cement is evident by the two curves on No. IV. The increase in the strength of the briquettes with greater fineness is decided. This means that the larger the proportion of cement flour the stronger the attachment possible between cement and grains of sand or other aggregate.

Curve Sheet V brings out the increase of tensile strength with increasing setting periods. The market

neat cement has a low strength at the end of a day, but jumps more rapidly than any of the finer grades during the first week, which increase continues also to the end of 28 days. The reground samples have higher and higher strengths at the end of the first day in the order of increasing fineness. Their increase during succeeding days is less rapid than is that of the market sample, and this becomes more noticeable the longer the period and the finer the grinding. With the 1:3 mixture, the increase in strength is more uniform, the actual pounds per square inch becoming greater the finer the cement, both at the end of 7 and 28 days. While with the neat cement the market sample attained the highest strength of the series at the end of 28 days, in the diluted samples the final strength is greater the finer the cement, with but one exception. It may be noticed that the strength of the weakest 1:3 briquette at the close of the 7 day period is greater than that of the weakest neat cement at the end of 24 hours.

SOUNDNESS.

Soundness tests developed no serious defects, each cement passing satisfactorily both normal and accelerated tests.

A decided difference in the working qualities of the various cements would be expected from the rapidly decreasing space of time required for the initial set. (Table IV.) It was found that the cement became stickier to the trowel and to the hands as fineness increased, and to an annoying extent in the finest grained samples. Likewise the rapidity of the initial set rendered working difficult. The finest samples required working down several times during the process of filling the molds for the tensile tests. A cement that sets in 5 or even 17 minutes as do the 9- and 14-hour samples can scarcely be expected to give the best of satisfaction in use.

It, of course, remains to be learned whether the results of a series of tests on a number of different cements will

substantiate the more decided tendencies brought out in these experiments. It seems highly probable, however, that certain of the more pronounced effects will be produced in every case.

Fine grinding produces a cement which sets more quickly and which attains a high strength in a shorter period of time with the same proportions. This fact is suggestive. If fine grinding simply renders active more of the inert portion of the cement clinker, which formerly served the function of sand, we have before us the question, whether to (1) grind finer and therefore use in cement work a lower proportion of cement and a correspondingly greater proportion of sand or other aggregate in order to obtain the strength and stability which requirements now specify; or (2) to continue to use the present proportions with the more finely ground cement, but produce work which attains a greater strength in a shorter length of time. In the latter case, for example, the rapid hardening would permit of the earlier removal of forms from concrete structures, a saving which is of course to be balanced against the extra cost of fine grinding. At the same time, the difficulty of working and handling the more active, finely pulverized cement would probably render this alternative unfeasible under present methods and standards.

Assuming that a greater degree of fineness may be economically possible from the cement manufacturer's standpoint, the first of the above suggested results would probably be the more practicable. Less cement would be required to give the same bonding power. Should it prove that the ultimate strength of finely ground cement is greater, this would tend towards the revision of present dimensional standards to meet imposed conditions. For example, a reinforced concrete floor to support itself and to bear a specified load must be of a certain calculated thickness to be safe. A saving of cement and an economy of space would be realized in the use of a less proportion of the bonding agent could the same strength be attained.

There is, again, another phase of the matter which

concerns more specifically the cement manufacturer. The best information goes to show that less than 50 per cent of our commercial Portland cement possesses cementing properties. The remaining more than one half is inert, although of presumably the same composition and constitution. In other words, our commercial article has already in it, when put upon the market, say 50 to 60 per cent of sand. This sand has been obtained, however, in, it would seem, the most roundabout and expensive manner imaginable. Limestone and shale have been quarried, finely pulverized, mixed, burned, and, finally, again ground, several intricate and costly processes, to produce Portland cement. 50 to 60 per cent of this article is sand, whose production has required substantially the same outlay as has the relatively paltry 30 to 40 per cent that really possesses cementing properties. The non-hydraulic coarser grains serve, then, as so much retarder which so regulates the speed of setting of the mass that the cement may be put to practical use. We, who do not fully understand the minutiae of the processes of manufacture nor the chemical technique of the setting and hardening of cements, may ask, why not grind the entire output of the kilns to such a fineness that every particle will possess hydraulicity, and then, if a retarder is necessary, which no doubt will be, add some inexpensive inert material from another source to take the place of those coarse particles which, in our present Portlands, we believe serve no other purpose?

It is appreciated that the cost of pulverizing hard clinker rises very rapidly with the increase in the fineness of the product desired. There is of course a limit of fineness beyond which an economic efficiency, in the present day mills and methods of operation, can not be maintained. The efficiency of the tube mills in such common use runs rapidly down as the particles become smaller and as the proportion of the excessively fine increases. To do the most efficient work any mill must be hindered the least possible amount by the retention of particles that have reached the desired degree of fineness. A step in advance

along this line is the application of some method of separating and removing the pulverized particles as soon as they have reached the desired degree of comminution.

The data reported in this paper have but served to open up a number of questions concerning which investigation may yield valuable information. Some may hesitate to accept the prediction of Dr. Michaelis, Jr.,* that our present Portland cement can not be improved or its efficiency increased by fine grinding. This may be literally true, but we do not understand by it that improvement cannot be expected by reduction of the coarser particles, not necessarily to a *greater* fineness than the cement proper already has, but to at least such a size that they themselves will possess active cementing qualities.

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*Journal Western Society Engineers, Vol. XII, No. 4, p. 459.

NOTE ON SOME FUSION CURVES.

BY

A. V. Bleininger, Champaign, Ill.

In the study of the chemistry and physics of ceramics the mechanism of the fusion processes is of vital importance. Yet our knowledge of these fundamental processes is exceedingly limited, which is due to the fact that we have continued to investigate complex conditions with so many variables that our equations have been far too few to solve them. It is high time that we modestly begin the study of the simpler relations and, after mastering them, proceed to the investigation of the more complicated systems. There is no reason why in this way we should not obtain in time a fairly accurate knowledge of the chemistry of clays.

We must expect to meet discouragement, however, for only by the most painstaking care in keeping the conditions constant will we be enabled to obtain consistent results. We must at all times remember that the reactions taking place in our clays are never completed but will always remain far from the end-point, and that they are dependent upon the conditions of the partial equilibrium reached. Evidently important factors are,—slow or rapid heating, crystalline or amorphous substances, etc.

Though we may not reach the most exact knowledge of the subject, by keeping as many conditions constant as possible we shall learn much from the correlation of melting-points and here, fortunately, the differentiation of melting point series is of greater help to us than the knowledeg of isolated melting points. In this way the maximum and minimum points are detected, and we are enabled to fix the temperatures at which chemical reactions take place, the fusion temperatures of the eutectic mixtures

and the compositions corresponding to these critical points. Usually, maximum points correspond to compounds and the minimum points to eutectic mixtures.

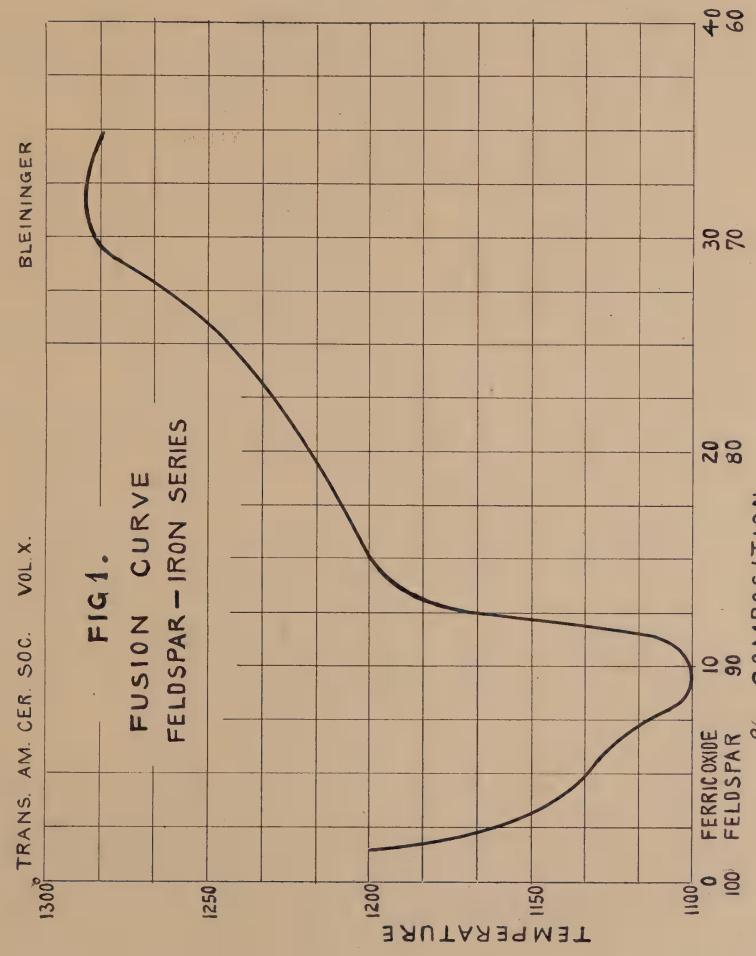
In the preliminary study of the fusion curves begun at the University of Illinois, the first work comprised mixtures of feldspar, ferric oxide and whiting, since these mixtures are of interest in the study of some of the Illinois clays. Commercial materials were used and it was found that, though the whiting appeared to be of good color and was bought as high-grade material it proved quite impure.

The composition of the feldspar, whiting and ferric oxide was found to be as follows:

	Silica	Alumina	Ferric Oxide	Lime	Magnesia	Potash	Soda
Feldspar	68.22	17.83	trace	0.30	0.11	12.13	1.90
Whiting	1.62	3.50	trace	52.65	trace	.....	....
Iron Oxide	.....	.....	99.00	.....	....	.....	....

These three constituents were ground together, dry, in a small ball mill, in various proportions, from 100% feldspar to 40% ferric oxide, 100% spar to 40% whiting and 100% spar to 40% ferric oxide plus whiting, in intervals from 1-5%. The interval was made small, close to 100% of feldspar, so as to bring out the effect of smaller amounts of either material upon feldspar. From 1% the interval was increased to 2, 3 and 5% as the feldspar diminished in amount.

The mixtures were then made up with dextrine water into a dough and molded into cones in a metal mold. After drying, the cones were placed on clay slabs, in duplicate rows and melted down in a coke-fired test kiln, having been protected from the flame by means of a high tile sagger which was partially open on the back and front. A thermocouple was placed as close to the cones as possible. Correction was made for the cold junction temperature. Through a thin piece of glass inserted in the spy hole the cones were watched with ease, and their going down ob-


TRANS. AM. CER. SOC. VOL X.
BLEININGER
FIG 1.
FUSION CURVE
FELDSPAR — IRON SERIES
TEMPERATURE
1300°
1250
1200
1150
1100
0 FERRIC OXIDE 10 20 30 40
100 FELDSPAR 90 80 70 60
% COMPOSITION

served by means of an opera glass. Unfortunately some of the cones were cracked in drying due to an excess of dextrine and broke off in the kiln. These were not considered in the result.

In Fig. 1 we have shown the fusion curve of the feldspar-ferric oxide series, and a eutectic is clearly indicated with 91% feldspar and 9% of iron oxide. This mixture corresponds to the formula:

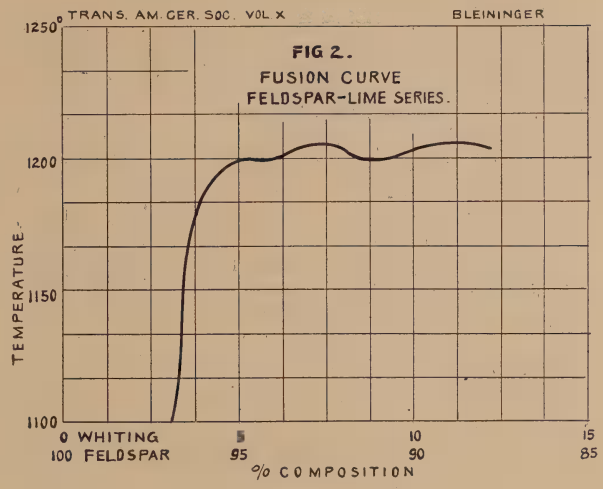
$$\left.\begin{matrix} 0.015\ MgO \\ 0.034\ CaO \\ 0.766\ K_2O \\ 0.185\ Na_2O \end{matrix}\right\} 1.04\ Al_2O_3 \left\{ 0.415\ Fe_2O_3 \right\} 6.82\ SiO_2$$

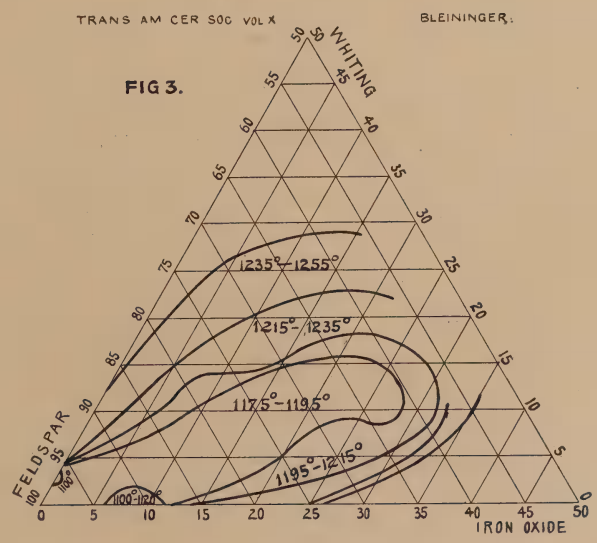
The feldspar formula is represented by the same formula but without the iron. This mixture therefore fuses at a lower temperature than the feldspar itself or any other mixture of the series.

In Fig. 2 the feldspar-lime series is not complete owing to the breaking of some of the cones, and hence the eutectic point is not definitely established, but it is quite evident that it is close to 97% feldspar, 3% whiting. This would correspond to a slight enriching of the spar in lime corresponding to about 0.03 equivalent. Since this point was not determined with certainty no interest is attached to its formula.

In Fig. 3 there are plotted the compositions of the mixtures in terms of the percentages of feldspar, iron-oxide and whiting, and it is evident that the isothermal compositions are connected by some definite law. Each curve represents a temperature interval of 20°, corresponding to the range of one cone. Thus every mixture in the inner area melted between 1175° and 1195° C. The increase in area indicates the enriching of the fusion by the solution of other materials on raising the temperature, and we learn thus in what direction this takes place.

Similar curves carried on very carefully with pure lead silicates, fusing the cones in an electric furnace, showed some disturbing factor owing to volatilization of the lead, and hence are not produced. This trouble was


TRANS. AM. CER. SOC. VOL X
BLEININGER
FIG 2.
FUSION CURVE
FELDSPAR-LIME SERIES.
TEMPERATURE
1250°
1200
1150
1100
0 WHITING
100 FELDSPAR
5
95
10
90
15
85
% COMPOSITION


TRANS AM CER SOC VOL X
BLEININGER
FIG 3.
WHITING
FELDSPAR
IRON OXIDE
1235°-1255°
1215°-1235°
1175°-1195°
1195°-1215°
1100°-1120°

encountered even with fritted glasses, and the work is to be repeated under special precautions.

DISCUSSION.

The Chair: I think Professor Bleininger has given us a splendid paper, and I am very glad to know that he is getting near to the practical man. I will call on Mr. Stover, as a practical man, to discuss the paper.

Mr. Stover: I would like to ask Professor Bleininger why he expressed the data in percentage weights?

Mr. Bleininger: Because it was the simplest way.

Mr. Stover: I don't want to say a word against the use of technical formulæ, for I sat up many nights in order to master it so I could figure them out by myself; but it is a fact that I have been arguing along the line of this sort of expression without much result until at this meeting. I have contended it would make it more simple, and if we could have the kind of data Mr. Bleininger has been trying to give us lying around in the mixing rooms of the practical potters in Trenton and East Liverpool, we would have something here in the pages of the proceedings which would be of practical value. But for the most part, we are soaring around over their heads and they cannot understand us. I am glad Professor Bleininger has put his data in plain percentages, for I believe it will be productive of practical results.

The Chair: I want to say, as a practical man, that I am impressed with the fact that we are getting closer and closer to the practical man in our work. There are many things about the technical part of the American Ceramic Society's work which the practical man cannot understand; but he realizes the meat is there even though he cannot always digest it. I think this is a simple method and that the practical man will by and by conclude that after all there is something in pottery worth knowing that he does not understand.

THE ACTION OF THE DIFFERENT FORMS OF CALCIUM AS A FLUX IN PORCELAIN MANUFACTURE.

BY

ARTHUR S. WATTS, Victor, N. Y.

Some time ago while in conversation with a practical potter I was asked for my experience with marble dust as a substitute for whiting. The impression seemed to prevail that it gave a whiter product. I could not imagine how marble could produce any different results than is obtained from whiting provided both have the same chemical composition and are reduced to the same degree of fineness. However, as I had never seen a series of porcelains in which the action of the different calcium fluxes are comparable, I was unable to make any statement. The only data which I could find along this line is an article by H. E. Ashley in Vol. VIII, Trans. A. C. S., pages 147-153. In this article Mr. Ashley gives some valuable data on "The Action of Lime in Earthenware Bodies," in which he compares the action of whiting and fluorspar as regards absorption, abrasion and translucency.

I decided to cover the same field in porcelain, but in order to make the paper more complete I decided to add $CaSO_4$ to the list and also to make a series using pulverized marble. In order to make the work as practical as possible I have used only the best grade of English China and Ball Clays and the best ground rock flint and spar.

The analyses of the Calcium Fluxes are as follows:

WHITING.

$CaCO_3$	.970
Silicious Residue	.021
Fe_2O_3	trace

PULVERIZED MARBLE.

$CaCO_3$	.7678
$MgCO_3$	.1716
Al_2O_3	.0064
Fe_2O_3	.00108
Silicious Residue	.0432

PLASTER OF PARIS.

$CaSO_4$	.946
$MgCO_3$	.016
Fe_2O_3	trace
Silicious Residue	.021

FLUORSPAR.

No complete analysis attempted but a titration for iron shows that only a trace is present.

I chose as the foundation of the series a good practical porcelain body of the following composition:

Series O —.16 K_2O : 1. Al_2O_3 : 4.5 SiO_2

which in percent weights is:

Feldspar	21.35
English China Clay	43.92
English Ball Clay	8.00
Flint	26.73

This gives at cones 10 to 12 a good white porcelain of splendid translucency and good color. The color could undoubtedly be improved by reducing the per cent of ball clay, but as it stands it is a good porcelain body. With this formula as a basis I made four series, viz.:

Series K—in which calcium will be introduced as whiting, ($CaCO_3$).

Series L—in which calcium will be introduced as pulverized marble, ($CaCO_3$, $MgCO_3$).

Series M—in which calcium will be introduced as plaster of Paris, ($CaSO_4$).

Series N—in which calcium will be introduced as fluorspar, (CaF).

Body O which will contain no calcium flux and which will be used as a standard to determine the extent of the action of the various added fluxes.

I am adding these fluxes to the standard body instead of substituting because in my judgment this is the only exact method by which we can compare their action.

From this O body I have developed the following range as uniform to every series:

K, L, M & N 1	.16 K_2O .16 CaO	1. Al_2O_3	4.5 SiO_2
K, L, M & N 2	.16 K_2O .12 CaO	1. Al_2O_3	4.5 SiO_2
K, L, M & N—3	.16 K_2O .08 CaO	1. Al_2O_3	4.5 SiO_2
K, L, M & N—5	.16 K_2O 04. CaO	1. Al_2O_3	4.5 SiO_2

To obtain the batch of the various series you have only to add "O" body as follows:

	No. 1	No. 2	No. 3	No. 4
In K Series add Whiting	3.83%	2.88%	1.92%	.96%
In L Series add Pulverized Marble...	3.60%	2.70%	1.80%	.90%
In M Series add Plaster of Paris....	6.58%	4.94%	3.30%	1.65%
In N Series add Fluorspar	3.00%	2.25%	1.50%	.75%

These series were made in the regular way by grinding in ball mills, lawning and filtering. The different batches were wrapped in wet cloths and allowed to soak for a couple of days before being made into test pieces. For test pieces I made up the materials into four different forms: 4 inch plates, 1 inch cubes, tensile test briquettes with 1 inch cross section and pyrometric cones. These latter were

to be made use of for preliminary firing in order that the work might be outlined before firing the regular test pieces.

I first fired, at cone 12, 3 sets of cones covering the complete series. This test was made under normal conditions, the burn being of 40 hours duration and the cooling being slow and as nearly as possible in neutral atmosphere.

The result was somewhat of a surprise. All the series of cones stood the fire of cone 12 withiut any evidence of bending, and save for a slightly glossier surface on some there was no difference in appearance between the different members of any of the series. However, when the test pieces were fired, N-1 bloated badly and N-2 showed some bloat. L-1 and L-2 also showed minute bloat, but in this series it appears as a few pimples only.

Regarding color, it is a question if any of the series is whiter than the others. After careful study and by calling on others for their opinion it was decided that L series was a trifle whiter than the other, but of the remainder any judgment might be contradicted. The K and M series display a very slight shading toward the lemon, while the N series shows a slight shading toward the brown. The series O cones which contain no lime cannot be distinguished from the others by color, so uniform is the entire set. The translucency of the series was studied and no conclusion could be reached. There is possibly a slightly increased translucency in the numbers highest in calcium, but the increase, if any, is very small.

Regarding brittleness, I would say that it is especially notable that the L and N series highest in calcium are markedly more brittle. As a general statement I should say that of the four series there is not enough difference to enable one to make a positive selection. None of these forms of calcium seems more active as a flux than the others under the conditions prevailing. It is evident, therefore, that with uniform firing and gradual cooling in neutral or very slightly oxidizing atmosphere, one form of calcium is as good as another.

However, should the firing be irregular or should a period of severe oxidation or reduction prevail, there might be a difference in their action and a pronounced superiority be indicated.

To determine this the test pieces were divided and one portion was subjected to a severe oxidizing burn while the other was subjected to a severe reducing burn.

OXIDIZING BURN.

This burn was made at cone 12, and to insure the color of iron being brought out as pronouncedly as possible, there was introduced into the burn several short reducing periods followed by severe oxidation. At the close of the firing, which was a standard 40 hour burn, the trials were cooled in as strongly oxidizing an atmosphere as was obtainable. For this reason the cooling period was somewhat shorter than on the neutral or reducing burn. The results of this burn are far in excess of my expectations.

Color. So far as color is concerned this burn has certainly brought results. All of the trials highest in calcium, viz., K-1, L-1, M-1 and N-1 are very pronouncedly yellow, while the higher numbers of the series which contain proportionately less calcium are nicely graduated in color scale, ending in the O series which is a very pale cream and by far the least affected of any of the series. The most pronounced yellow color is displayed by the M Series which carries the plaster of Paris. This is followed in order by the N series carrying the fluorspar, the K series carrying the whiting and last the L series carrying the pulverized marble.

Condition of trials. Even more pronounced than the color is the condition of the trials. There is a notable increase in size of every series indicating that either minute bloating has occurred or that the shrinkage has been reduced.

The increase in size is most pronounced in the N series where bloating has undoubtedly occurred. N-1 of this

series shows a notable bloating, the entire mass being swollen and slightly distorted. The bloating and size decrease uniformly in the higher numbers of the N series until in N-4 we find the bloat reduced to a satin-like surface and the size 25% less than N-1.

Series K and L are next in order of size, and are very nearly the same in this respect. No bloating is apparent in series K, but both L-1 and L-2 have a few small bloat bubbles and L-3 has a few spots that possibly are minute bubbles. The bloat in this series does not affect the entire mass to distort it as is the case in series N, but displays itself as isolated bubbles which are well defined.

Series M seems to be affected least of any so far as changed size is concerned, but shows a few isolated bubbles on M-1 and a reduced number on series M-2. M-3 and M-4 are smooth and clean.

General Conclusion. In general conclusion of this burn I would say that, in my judgment, the bloat observed was the direct result of the reducing action resorted to in order to get the flashing effect desired to bring out the color. That complete reduction was followed by complete oxidation is certain since the trials show the same color through their entire cross-section when broken in the tensile test. So severe a conditions as this would not likely prevail in ordinary work, but should you put on a very heavy fire near the finish without first cleaning your grates to permit of a free draft, you might obtain for a time a condition which, on the return to oxidizing atmosphere, would produce identically this color and condition on the surface and perhaps throughout thin ware.

REDUCING BURN.

This set of trials was necessarily fired under oxidizing conditions until a good cherry red heat was reached, when the draft was cut back and just as little excess air was passed into the kiln as was necessary to maintain an increasing temperature. Every precaution possible was taken

to prevent a flash of oxidation at the finish. When the desired temperature was reached and the fires burned clean and clear, all drafts were closed and a reducing atmosphere was maintained during a slow cooling period. The temperature reached in this burn was only cone 10 flat, but on account of other ware in the kiln it was not considered advisable to go higher with such severe reducing conditions prevailing.

The results are as pronounced and as interesting as were noted in the oxidized burn and as little to be expected.

Color. Instead of the pale cream white noted in the neutral burn or the pronounced yellow of the oxidizing burn, we now have a pronounced blue white. This is shown most prominently by the N series in which N-1 displays a pronounced blue stone color such as is noted in vitrified buff clay. N-2 displays this blue-stoning less intensely and N-3 and N-4 shade up to a good blue white.

Series L is next to N in degree of color, followed in order by K with M least affected. The intensity of color in the members of each series decreases proportionately as the content of lime decreases until in K-4, L-4, M-4 and N-4 we have very little more of the blue tendency than is displayed by the O body in which there is no calcium.

Regarding the color of these trials, I would say that, in my judgment, and by comparison with other porcelains, K-2, 3 and 4, L-2, 3 and 4 and M-2, 3 and 4 in the reducing burn, are all superior to O as regards whiteness of color, since O displays even under reducing conditions a trace of cream color. N-4 might be included in this lot also, but I think its texture would condemn it as I will explain later.

Texture and Shrinkage. In this burn the variation in size is not nearly so pronounced as in the oxidized burn. Series N is again the largest of the series and is followed in order by series K, series L and series M. The texture and vitrification of this set of trials is very interesting.

Series N has undoubtedly insipient bloat since its surface is not dissimilar to series N under the oxidizing burn, except that there is no evidence of distortion.

N-1 has a dry rough surface.

N-2 has a peculiar egg shell surface such as we sometimes find in bone china.

N-3 shows a slight gloss and less of the egg shell effect.

N-4 is quite glossy and smooth, but still shows a trace of the egg shell surface.

Series L undoubtedly is the next in order of vitrification since its surfaces are all bright.

L-1 shows fine sharp corners but is highly self-glazed.

L-2 is a trifle less glossy than L-1 and less self-glazed.

L-3 shows a fine smooth surface and but little evidence of self-glaze.

L-4 is a very highly vitrified piece of porcelain but without any evidence of self-glaze.

M series is next in order, but only in M-1 is there any evidence of self-glazing.

M-2 shows a fine smooth surface but little gloss, while M-3 shows a decreasing degree of vitrification.

M-4 is a dry vitreous surface without gloss.

K series is last in order, and only by close study can you detect any shine on the surface of any of this series.

K-1 shows a trace of gloss, while K-2 is as dry surfaced as M-4. K-3 and K-4 are dry hard porcelains.

Series O is a smooth hard porcelain, which appears intensely white until brought in contrast with some of the series which display a pronounced blue color.

UNIFORM TESTS ON ENTIRE SERIES.

I now decided to determine the moisture, shrinkage and specific gravity on the various trials, and I present a table in which the results of the various determinations are set down:

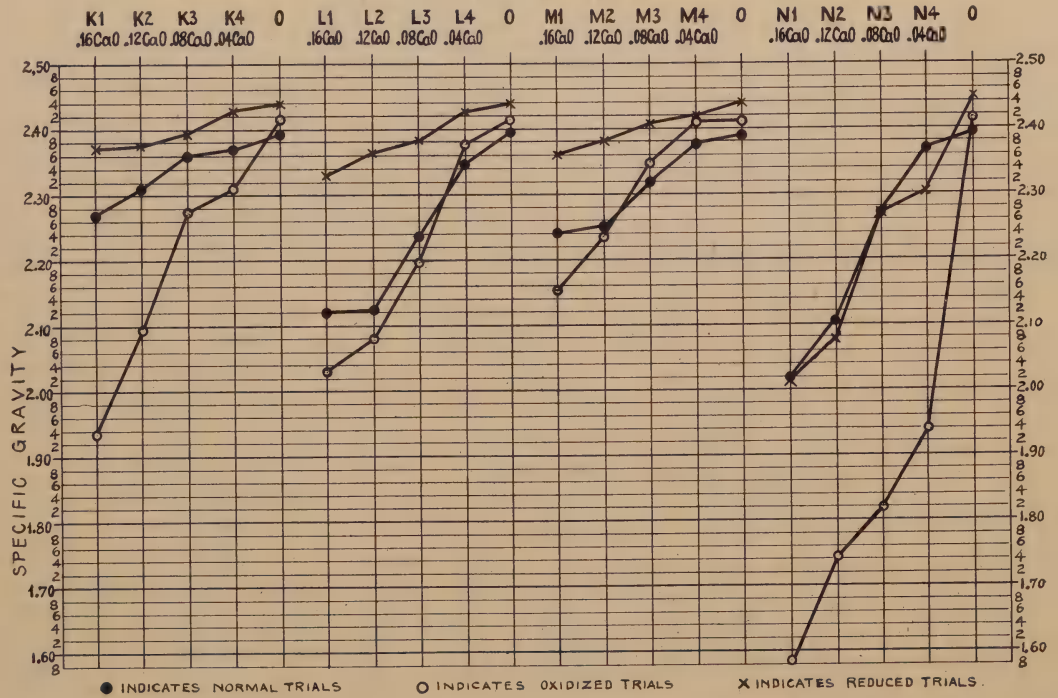
TABLE OF SPECIFIC GRAVITY, SHRINKAGE AND ABSORPTION, SHOWING EFFECT OF VARIROUS LIME FLUXES. UNDER DIFFERENT KILN CONDITIONS.

	OXIDIZED			NORMAL			REDUCED		
	Specific Gravity	Shrinkage	Absorbtion	Syecific Gravity	Shrinkage	Absorbtion	Specific Gravity	Shrinkage	Absorbtion
K 1..	1.9366	10.43%	.—%	2.2700	15.70%	.—%	2.3706	15.74%	.—%
K 2..	2.0949	11.49%	.—%	2.3123	15.87%	.—%	2.3775	16.02%	.—%
K 3..	2.2726	13.94%	.—%	2.3599	15.87%	.—%	2.3967	16.73%	.—%
K 4..	2.30505	14.93%	.—%	2.3720	15.93%	.—%	2.4277	17.58%	.—%
L 1..	1.9293	10.58%	.102%	2.1218	15.34%	.—%	2.3319	17.13%	.—%
L 2..	2.1003	11.98%	.072%	2.1242	15.46%	.—%	2.3659	17.13%	.—%
L 3..	2.1977	12.83%	.051%	2.2339	15.58%	.—%	2.3836	17.58%	.—%
L 4..	2.3747	15.74%	.—%	2.3499	15.99%	.—%	2.4280	18.45%	.—%
M 1..	2.1556	15.74%	.—%	2.2409	15.99%	.—%	2.3598	17.78%	.—%
M 2..	2.2344	15.85%	.—%	2.2445	16.37%	.—%	2.3817	17.44%	.—%
M 3..	2.3451	16.73%	.—%	2.3208	16.67%	.—%	2.4052	17.13%	.—%
M 4..	2.4152	17.28%	.—%	2.3777	17.13%	.—%	2.4182	17.13%	.—%
N 1..	1.5864	7.59%	.426%	2.0335	15.02%	.—%	2.0283	12.52%	.—%
N 2..	1.7428	11.30%	.192%	2.1032	15.24%	.—%	2.0785	13.19%	.—%
N 3..	1.8280	12.16%	.118%	2.2673	15.46%	.—%	2.2677	16.20%	.—%
N 4..	1.9391	12.52%	.046%	2.3626	15.87%	.—%	2.3088	16.42%	.—%
O.....	2.4140	17.39%	.—%	2.3963	17.13%	.—%	2.4426	16.97%	.—%

Moisture. The moisture determination was made by soaking the test pieces for 48 hours in water maintained at just below the boiling point. You will notice that only in the oxidized trials is there any evidence of absorption. The N series shows the greatest absorption, N-1 absorbing .426% moisture, which in N-4 is reduced to .046%. The L series is the only other series showing any absorption, and in the maximum case of L-1 it only shows .10%.

Shrinkage. The shrinkage trials are taken by measurement, and where the difference is so small as is the case with a series of porcelains, there is always a possibility of error. However, the record is in every case an average of four measurements except in the normal burn, of which I had only one set of measurements.

CURVES SHOWING THE EFFECT OF THE VARIOUS LIME FLUXES ON SPECIFIC GRAVITY.



Specific Gravity. In this I think I find the most reliable means of measuring and comparing, since the ordinary factors of warped test pieces, uneven finishing, etc., which makes the shrinkage determinations so unsatisfactory, do not enter. The data on specific gravity as here offered is the result of two complete sets checked by duplicate weighings.

Note how widely varied are the specific gravities of the oxidized trials, how they invariably draw into a narrower area in the normal and are, except in the case of the N series, still closer together in the reduced trials. This is well shown in the accompanying plot in which I have tried to show by comparable curves the range covered by the different compounds under the three different heat conditions. Comparing the range of specific gravity for the different series, we see that Series M is decidedly the best of the lot, as its variation, where .16 equivalent of calcium is used, is only .20 over the entire range, while with .04 CaO used, the maximum variation of its specific gravity is only .04.

Series L comes next in this respect with a maximum variation posisble in L-1 of .41 in specific gravity and a maximum variation in specific gravity of L-4 of .0781.

Series K comes next in order with a maximum specific gravity variation in K-1 of .434, while the maximum variation of K-4 is .12.

Series N has the greatest variation of any of the series and yet its variation under the various heat treatments is not nearly so great as one would expect to find on examining the trials. Its maximum specific gravity variation in N-1 is only .442, which is practically the same as we find in K series. Its minimum in N-4 is, however, .4235, showing that when present even in small quantities, it does its work.

"O" Body under the various treatments has a maximum specific gravity range of .0463. Note also that its lowest specific gravity is displayed in the normal trials. This quality is displayed also by L-4 and M-3 and M-4. For this phenomenon I can offer no explanation. In general,

this set of data indicates that at least under the conditions to which these trials have been subjected, the ware becomes heavier on reduction. This does not indicate that there was the degree of gas absorption ordinarily to be expected. My explanation for this is the fact that the slow cooling allowed the gradual expulsion of gas as the mass contracted, while the rapid cooling made necessary by the oxidizing atmosphere demanded caused the surface to harden and prevent the escape of the gases.

I have one more table to offer, i. e., A Table of Comparable Tensile Strengths under the two Extreme Conditions.

As you will note on examination there is a notably greater strength displayed by the reduced trials than we find in the oxidized trials. The tendency to bloat is apparently to blame for much of this weakness, and if you will compare this table with the specific gravity table you will find that the same trials that show the highest specific gravity, with a few exceptions show, the greatest tensile strength. In the oxidized trials M-1 has the highest specific gravity of any of the trials carrying .16 CaO, and it also has the greatest tensile strength of any of the No. 1 trials. M-2 stands highest under the same examination, as does also M-3.

M-4 seems for some reason to have fallen down, as all its tensile tests are uniformly low. Later work will possibly explain or correct this irregularity.

Of the reduced trials K-1 stands at the head of the No. 1 trials with 1750 lbs. strength and 2.37 specific gravity. K-2 has 2.3775 specific gravity and 1800 lbs. tensile strength; L-3 has 2.3836 specific gravity with 1925 lbs.; K-4 shows 2.4277 specific gravity with 2375 lbs.

In this comparison the highest in tensile strength is not invariably the highest in specific gravity, but the tendency seems to be that way except with the $CaSO_4$ series. On studying series M we find its greatest strength displayed under the oxidizing conditions, which is exactly the reverse of what we find in the other three tables. Note

TABLE OF TENSILE STRENGTHS, SHOWING EFFECT OF VARIOUS LIME FLUXES UNDER DIFFERENT KILN CONDITIONS.

All Tests on Approximately One Square Inch.

	FIRED UNDER OXIDIZING CONDITIONS		FIRED UNDER REDUCING CONDITIONS		FIRED UNDER NORMAL CONDITIONS	
	Tests Per Sq. In.	Average lbs.	Tests Per Sp. In.	Average lbs.	Tests Per Sq. In.	Average lbs.
K 1..	1050 —1200—1250—1400 lbs.	1225	1450 —1750—1800—2100 lbs.	1750	2100— 2200 lbs.	2150
K 2..	1200 —1200—1300—1300 lbs.	1250	1800 —1800—1800—1800 lbs.	1800	2100— 2100 lbs.	2100
K 3..	1300 —1400—1550—1650 lbs.	1475	1250 —1450—1500 1700 lbs.	1475	1850— 2350 lbs.	2100
K 4..	1600 —1700—1800—1800 lbs.	1725	2250 —2400—2400—2450 lbs.	2375	2200— 2550 lbs.	2375
L 1..	1000 —1000—1200—1200 lbs.	1100	1650 —1650—1650—1750 lbs.	1675	1400— 2200 lbs.	1800
L 2..	1200 —1300—1300—1300 lbs.	1275	1200*—2000—2100—2450 lbs.	1937	*1100— 1500 lbs.	1300
L 3..	1450 —1450—1450—1450 lbs.	1450	1700 —1800—2000—2200 lbs.	1925	1550— 1750 lbs.	1650
L 4..	1350 —1400—1400—1550 lbs.	1425	1650 —2000—2050—2300 lbs.	2000	2100— 2450 lbs.	2275
M 1..	1800 —1850—1850—1850 lbs.	1837	1450 —1550—1650—1650 lbs.	1575	1900— 1900 lbs.	1900
M 2.	1600*—1750—1800—1950 lbs.	1775	1150*—1400—1500—1650 lbs.	1475	1500— 1850 lbs.	1675
M 3.	1700 —2000—2200—2300 lbs.	2050	1050 —1300—1350—1800 lbs.	1375	1600—*1700 lbs.	1650
M 4.	1300 —1350—1350—1400 lbs.	1350	1100 —1400—1400—1500 lbs.	1350	2050— 2100 lbs.	2075
N 1..	800 — 800— 850— 850 lbs.	825	800 — 850— 950—1100 lbs.	925	800— 1150 lbs.	975
N 2..	950 —1050—1050—1050 lbs.	1025	850 —1100—1250—1500 lbs.	1175	900— 1500 lbs.	1200
N 3.	1050 —1300—1300—1500 lbs.	1300	1450 —1500—1700—1750 lbs.	1600	1150— 1500 lbs.	1325
N 4..	850 — 850— 850— 900 lbs.	862	1050*—1400—1500—1500 lbs.	1362	1050— 1350 lbs.	1200
O	1900 —1900—2000—2000 lbs.	1950	2100 —2150—2200—2200 lbs.	2162	2100— 2150 lbs.	2125

Note—*Indicates a flaw displayed by the broken briquette.

also that the strength of the M series under reducing conditions increases as the amount of $CaSO_4$ increases. Just the reverse is the case with every other series. As you can readily understand, it is impossible to form any reliable scale with so few trials, and I am only endeavoring to draw out what is indicated by the tests at hand.

CONCLUSIONS.

In concluding this paper I desire to say that, in my judgment, it brings out three facts, viz.: (1) That more variation is to be expected where any quantity of calcium flux is added than where a plain feldspar body is manufactured. (2) That a small addition of calcium flux may improve color if properly handled. (3) That we do not find all the desirable qualities in any one body. For example:

For whiteness under normal or average conditions series L would be chosen. For mechanical strength under reducing conditions I believe the K series has the advantage, while under oxidizing conditions the M series is undoubtedly far ahead.

The N series is undoubtedly to be condemned for use since it appears faulty under any other than ideal conditions. My explanation for this tendency is that its action begins so early in the burn that the clays and spar of the body have not shrunk sufficiently to form a close body and thus it invites an excessive absorption of gas, which later may be expelled by careful cooling, but which nevertheless has done its work of discoloration.

Another lesson of this paper, if its data has any value, lies in the fact that by its guide we would conclude that with a calcium flux not carrying over .1% of Fe_2O_3 we may go as high as .08 CaO or even .12 CaO introduced as either whiting or pulverized marble without experiencing any trouble from color if the biscuit kiln is finished and cooled under any other than strongly oxidizing conditions. However, if $CaSO_4$ is used, the ware, under above conditions, may be expected to be weak mechanically, and to

counteract this tendency an oxidizing atmosphere must be resorted to even at the sacrifice of color.

So it appears that each body requires its own especial treatment, depending on its composition and inherent tendencies and only by knowledge of, and consideration for, these tendencies may we hope for success.

DISCUSSION.

Mr. Stover: I did not expect to occupy first position in discussion of this paper, but I want to give my personal thanks to Mr. Watts, and to express to him my apprecation of the fact of his coming round to the practical man's way of thinking, as indicated by his putting in the percentage weights. We have been having discussion of this question for several years; but when Mr. Watts comes around and puts in batch weights, I begin to think you are coming around to my constant argument to put our papers and discussion also in an intelligible form for the practical man.

Mr. Binns: One thing has occurred to me with regard to Series "N." I want to know whether Mr. Watts took any account of fluorine? I am disposed to think the blistering is due to fluorine.

Mr. Watts: Fluorine is of course considered in introducing fluorspar. How could you use fluorspar without getting fluorine?

Mr. Binns: You could not, but why do you take no account of it in the development of this blister?

Mr. Watts: I don't know that I mentioned that fluorspar might have caused the blister, but the fluorspar series was condemned as a whole because only under ideal conditions did it result in good porcelain. If it was heated up and cooled very slowly there was but little blistering. There was some blistering under absolutely normal conditions in the series having .16 of fluorspar. With a small amount of fluorspar we got a fine white body without evidence of blistering. I am disposed to think the bloating

was the effect of the calcium or calcium compounds, largely depending on the form used. I think that we cannot consider the action of calcium alone without considering the sources from which it is derived. In my opinion that is a highly important point.

Mr. Purdy: All the results give curves which are very significant in the facts they show. I am an advocate of that method of experimenting. With no calcium carbonate he had the maximum density; that is, maximum density of that portion of the piece which was impervious to water. He saturated his saucer with water, so that data here gives the density of the solid portion. With the increase of lime we get decrease in specific gravity; in other words, decrease in density. This decrease in density is due in part to bleb structure. We call it vesicular structure,—it is a porous system into which water cannot get.

The most remarkable fact shown here is, that under oxidizing conditions he gets the largest development of vesicular structure and under reducing conditions the least development of vesicular structure. Why should the gases that are evolved wish to leave the body more vigorously and evidently under higher pressure under oxidizing than under reducing conditions? Of course, there are possible explanations of that, but to that fact and the explanation that might be given, I desire to draw attention in this case. I think Mr. Watts has shown some important and interesting lessons which can be brought out by the specific gravity curve, and the influence of acids, and of oxidizing and reducing conditions, is nicely shown on the charts; and I hope to have an opportunity to discuss it further before publication.

Mr. Binns: I would like to ask Professor Purdy whether he gives it as his opinion that the increased vesicular structure of the two mixes which contain calcium carbonate is due to CO_2, and how he proves it. As I understand it, CO_2 leaves the body immediately after dehydration.

Mr. Purdy: I put a question similar to that in regard

to free water which a mineralogist wanted me to believe was in igneous rocks. Pure quartz crystal slides when tilted show particles of water much like the spirit in a level. Under the heat at which that rock was in a molten condition, there ought to have been no water, but there it is.

Mr. Binns: The point of analogy is not complete. It is familiar to all of us that CO_2 can be enclosed in a glaze structure, because being locked in the fluid, it has no chance to escape; but where the body is brought up from a porous condition, I think the condition is very different. I do not think the CO_2 from the calcium carbonate could remain.

Mr. Purdy: When fusion has progressed so far that the clay has reached that stage known as vitrification, the clay is in a condition similar to that of taffy at summer heat. Any gases which are being set free at this time will be prevented from escaping simply because the avenues of escape have been closed. Now how early in the burning is this condition reached? In the work presented to you by Moore and myself last year we showed that in No. 1 fire clays this was undoubtedly reached at cone 1 to 3 and in the more fusible clays much earlier. Absolute closing up of the pore is not necessary before such a conditions of affairs can exist. It is only necessary that a small portion of the mineral ingredient should have attained this taffy-like condition.

Now in a vitrifying body we undoubtedly have a condition of affairs that is favorable to the development of pressure within the ware. Under pressure, dissociation proceeds less rapidly and resistance to dissociation increases with increase of pressure. If sufficient pressure is maintained you can heat calcium carbonate a high as you can and still have no dissociation. In fact, temperature is only one of the factors that effect dissociations. Pressure can completely annul the effect of temperature. This is not theory but fact fully demonstrated and understood by physicists.

If there is any pressure within a vitrifying piece of

clay, it is more likely caused by expanding gases that can not freely escape. "Blowing up" clay wares during drying is sufficient evidence of pressure that can be caused by expanding gases. From the beginning of the drying to the time the clay has been given its "finishing heat" gases of one kind or another are escaping.

There are several things which are volatilized from clay, principally, water, acids which are being displaced by silica, and the alkalies. Under the combined influence of pressure and temperature the dissociation and expulsion of these evolved gases may extend over the entire heat range used in ceramic burning.

Mr. Binns: One more point: The temperature of cone 06 is 1030 degrees C. Do you know the temperature at which CO_2 is expelled from calcium carbonate?

Mr. Purdy: Yes, sir. Dissociation of calcium carbonate at atmospheric pressure can take place at temperature as low as 900 degrees.

Mr. Binns: Then by the time cone 06 is reached all the CO_2 has been expelled.

Mr. Parmelee: I understand the specific gravity was determined by immersion and loss of weight on suspension, on the whole piece. May I suggest that Mr. Watts should include in his paper the specific gravity of the powder of a crushed piece? The surface of a piece of ware of that kind may be of a different character from the interior. We can settle the real specific gravity in that way.

Mr. Watts: I did not take the whole plate. I took pieces and determined the moisture on small pieces broken up, and which had been boiled about 24 hours—kept at almost the boiling temperature in water. These were used for specific gravity determination.

Mr. Stover: When you called for the opinions of the practical men, I was impressed with the silence which fell at that time. This society has stood for such high science that it has not drawn the practical men to the meetings. I will say to the young men attending if you want to have the practical men attend, you must express your papers

not only in chemical formulæ, but like Mr. Watts has done in this case, so the practical men can read the papers, make experimnets and come to the meetings with papers of vital importance. It will add to the value of our work to the industries if we have every paper accompanied by batch weights, so the practical men can prove up on them. If the man who is preparing the paper does not want to put them down, we ought to have some one appointed to figure them out for publication. By this means, I believe in five or ten years the value of our society would be beyond our expectations, if the papers were put in that shape.

Mr. Purdy: (Written since the meeting)

In this paper by Arthur S. Watts, data are presented which indicate that porcelains vary in strength with variation in apparent density. Since apparent density of burned ceramic ware is the density of the skeleton of the ware, it is obvious that the sealed cavities into which water cannot be made to enter affect very materially the apparent density. I made an investigation to determine what percentage part by volume of the skeleton of the several porcelains studied by Watts was sealed cavities or void spaces, and to analyze the data in order to determine whether a direct influence of the sealed cavities and molecular volume changes on strength of porcelain can be observed.

Volume Changes Due to Fusion:

In burning ceramic ware there are changes in volume other than that of the ware as a whole. Ordinarily we think of fire shrinkage of the outside dimensions as being the largest and most important volume changes that occur. In many cases this may be so, but in others it is not. In extreme cases there is such a decided bloating that the increase in volume of the sealed pores is obviously quite considerable and often so extensive as to cause an increase in exterior dimensions of the ware. There are also increases and decreases in molecular volume of the mineral constituents of the clay, which according to Roth may in

extreme cases amount to fifteen percent. If minerals retain this phenomena of changing in molecular volume when either mutually disolving one another or combining to form new compounds, as we know they do when fused together, then this must be considered as a very important volume change. Since neither the alteration in volume of the sealed pores or alteration in volume of the solid materials have any consideration in "fire shrinkage" data, it is plain that they should be investigated. It is not improbable that it will be found in future work that it is of more importance to make these internal volume measurements than the external volume measurements. Thoughtful consideration of what part of the mass gives shape, strength, and the other physical properties to wares leads one to believe that much will be learned from such studies.

THE SKELETON.

Density of Skeleton:

In a normally burned porcelain ware there are three distinct and measureable internal volumes which, combined, make up the external volume. These are (a) volume of the open pores, (b) volume of the sealed pores, (c) volum of the solid material. The skeleton of the ware is made up of the solid material and sealed pores. The skeleton is the portion of a saturated piece not occupied by water. Evidently, when the weight per unit volume (specific gravity) of this skeleton is made, we simply have the weight of material which actually occupies the unit volume. We do not have the weight of material which *can* occupy the unitv olume, because under ordinary conditions the skeleton as it stands embraces inclosed or sealed void spaces. The specific gravity of the skeleton thus obtained is therefore only *apparently* that of the solid material, hence the expression "apparent specific gravity."

The density of solid material in the skeleton cannot be determined until the sealed pores have been eliminated. It is plain that this can only be done by crushing the ware

to a powder and then determining the density of the powder.

Structure of the Skeleton:

The difference between the density of the powdered skeleton and its apparent density gives the weight of solid material that would be required to fill the sealed cavities. Consider two rubber balls having the same external dimensions, one being solid and the other hollow. The difference in the weights of these balls is the weight of rubber that would be required to make the hollow ball solid. This difference in weights in case of the rubber balls is analogous to the difference between the true density of the solid material and the apparent density of the skeleton.

Volume Changes within the Skeleton:

Since with increasing heat treatment and without loss in weight, most ceramic mixtures show a decrease in apparent density, it is safe to affirm that either (a) the mineral constituents comprising solid portions of the skeleton are undergoing an increase in molecular volume without an accompanying increase in volume of the void spaces, or (b) the void spaces within the skeleton alone are increasing in volume, or (c) that both of these volumes changes are taking place simultaneously. Recent writers credit most of the increase in volume of the skeleton to molecular alterations within the solid material. The writer has contended (but without sufficient data to support his contentions) that the larger part of the observed increase in volume of the skeleton was due to increase in volume of the inclosed void spaces. The writer's contentions in this matter are supported by results of a few determinations, in few of which there was *not* a very marked difference between the true densities of the powdered raw clay and powdered burned ware, and in others of which the dnsity of the burned powder actually exceeded that of the clay. Microscopic examination of slides cut from clay ware burned with sucecssively increasing heat treatment

have invariably shown a gradual increase in size of the sealed pores. The writer believes that because crystalline materials decrease in density (hence increase in volume) when calcined separately, it need not follow that the same minerals when fused together will show similar decrease in density. Our literature, however, does not contain data which would allow of positive claims for either contention.

METHODS OF DETERMINING VOLUMES.

Exterior Volume of Ware:

The direct measurement of the exterior volume of wares in a volumeter is now commonly understood. The indirect measurement which involves the "Principle of Archimides" that materials suspended in water appear to lose in weight the weight of an equal volume of water, is less understood. This latter method was used in the experiments here reported.

The difference between the dry weight of clay ware and weight when suspended in water is, by this principle, equivalent (in metric system) to the volume of the skeleton. That this is true is made plain when it is recalled that the dry weight of a piece is really the weight of the skeleton and that when saturated, the saturating water serves to buoy up and decrease its apparent weight just as much as will water out beyond its exterior surfaces.

The difference between the weight of the piece when saturated and the apparent weight when suspended in water is equivalent (in metric system) to the exterior volume of the piece. That this is so can be demonstrated algebraically as follows: If W is the wet weight; D, the dry weight and S the suspended weight, then W-D is the weight of water required to fill the open pores which, in the metric system, is equivalent to the volume of the pores. In the preceding paragraph it was demonstrated that D-S is equivalent to the volume of the skeleton. The total or

exterior volume is equal to the volume of pores plus volume of skeleton or

$$(W—D)+(D—S) \text{ which is equal to}$$
$$W—S \quad \text{Q. E. D.}$$

Sealed Pores:

In previous paragraphs it was explained that the weight of solid material which would be required to fill the sealed void spaces, is equal to the difference between the true and apparent weights per unit volume of the solid material in the skeleton. When this weight is compared with the weight of a unit volume of the solid, we are dealing with weights of the same substances, hence these weights are in the same proportion as the corresponding volumes of solid material. Then if T is the true density and A the apparent density of the skeleton $\left(\frac{T - A}{T}\right)100$ would give the percentage part of volume of the skeleton, which is occupied by the void spaces, and $\left(\frac{T - A}{T}\right)(D—S)$ would be the actual volume of the sealed cavities in a given piece.

DATA AND CALCULATIONS.

Specific Gravity:

In the following table are the data representing the apparent and true densities of the Watts porcelains:

TABLE I.
Apparent and True Densities.

	Apparent Specific Gravity			True Specific Gravity		
	Oxidized	Normal	Reduced	Oxidized	Normal	Reduced
K 1 3.83% Whiting	1.94	2.27	2.37	2.30	2.44	2.50
K 3 1.92% Whiting	2.27	2.36	2.40	2.29	....	2.47
L 1 3.60% Marble	1.93	2.12	2.33	2.46	2.38	2.38
L 3 1.80% Marble	2.20	2.23	2.38	2.47	2.47	2.45
M 1 6.58% Plaster of Paris...	2.16	2.24	2.36	2.48	2.50	2.46
M 3 3.30% Plaster of Paris...	2.35	2.32	2.41	2.60	2.62	2.64
N 1 3.00% Fluorspar	1.59	2.03	2.03	2.50	2.64	2.55
N 3 1.50% Fluorspar	1.74	2.10	2.08	2.64	....	2.58
O No lime flux	2.41	2.40	2.44	2.63	2.66	2.66

The apparent densities were determined by Watts and calculated on the formula $\left(\frac{D}{D-S}\right)$, which gives the weight per unit volume for the skeleton.

The true densities were determined by the writer. The test pieces were crushed in an iron mortar to pass a sixty mesh screen and the iron splinters removed by a magnet. Forty grams of the powder were carefully weighed out and placed into a graduated 200 cc. flask. Water then was run from a graduated burette into the flask and the volume occupied by the forty grams of powder determined by the difference between 200 cc. and the cubic centimeters required to fill the flask to the 200 cc. mark. 40 divided by the volume so obtained was taken as the true specific gravity of the solid material in the porcelains.

Percentage Void Space:

In the following table is given the percentage of the volume of skeleton which consists of void. These data were calculated on the formula $\left(\frac{T-A}{T}\right)100$ in which T is the true density and A the apparent density.

TABLE II.

Percent. Void Space in Skeleton.

	Oxidized	Normal	Reduced	Tensile Strength		
				Ozidized	Normal	Reduced
K 1	15.65	6.97	5.2	1225	1750	2150
K 3	0.88	.....	2.83	1475	1475	2100
L 1	21.5	10.9	2.10	1100	1675	1800
L 3	10.8	9.74	2.85	1450	1925	1650
M 1	12.9	10.40	4.80	1837	1575	190c
M 3	9.6	11.00	8.70	2050	1375	1650
N 1	36.4	23.10	20.4	825	925	975
N 3	34.0	.....	19.3	1300	1600	1325
O	8.4	9.8	8.3	1950	2162	2125

RESULTS.

Since sample marked O is the base mix containng no lime flux, its data may be used as a standard by which the meaning of the others may be interpreted.

Molecular Volume:

(1) It will be noticed that although all the lime fluxes here added have greater density than have the materials in the base mix, the true density of the burned powder is lower than that of the base.

(2) That the larger the amount of flux in each case, the greater is this decrease in density.

(3) That the true density of the unfluxed base is not less than that of the unburned ingredient from which it was made.

(4) Assuming that the true density of the burned base mix differs but little, if any, from that of raw mix, the percentage increaes in volume due to molecular alterations were calculated. The data obtained from these calculations are shown in Table III.

TABLE III.

Probable Percent: Increase in Volume of Solid Material Due to Molecular Alterations.

	Oxidized	Normal	Reduced
K 1	12.5	8.3	6.00
K 3	12.9	....	7.15
L 1	6.5	10.5	10.38
L 3	6.1	7.15	7.90
M 1	5.7	6.00	7.50
M 3	1.14	1.50	0.75
N 1	4.95	0.75	4.13
N 3	none	....	3.00
O	none	none	none

The data representing the percentage increase in volume cannot be compared with those for percentage volume of sealed voids, for the former represents the increase in volume over that which the material had when not burned and the latter the fractional part of the volume as it is in the burned ware.

The percentages of increase in volume shown in Table III are much larger than the writer had expected to find. If the powder had been reduced so as to pass a 100-mesh screen these percentages would no doubt be materially reduced. Further discussion of these results would not be worth while or hardly possible other than to note that they indicate that considerable of value may be had from similar data, if obtained under conditions that leave no doubt as to their accuracy.

Development of Sealed Voids:

The true significance of the data for percentages of sealed voids is appreciated only when it is considered that these porcelains have practically no open pores. The highest absorption reported by Watts was in case of N-1 (oxidized), which amounted to 0.42%. This being the case, the porcelains are practically 100% skeleton, and the

percentages given in Table II are the percentages of the whole or exterior volume taken up by the sealed void spaces.

From microscopic studies it has repeatedly been determined that the sealed pores increase in individual volume and in numbers as fusion progresses through that indefinite and ill-named period known as vitrification. The causes for sealed cavities are various, but whatever the causes may be it has been made evident by other data, and strongly emphasized by those data which are shown in Table II, that the increase in percentage volume of the sealed pores is as significant in effect on the resultant product as the decrease in percentage volume in open pores.

It is extremely doubtful if any of the porcelains tested by Watts had 20 to 30 per cent. by volume of sealed pores. Such a highly porous mass would not be suspected from their appearance. It must be that the pieces were not completely saturated before their suspended weights were determined. That this is very probable is shown by the fact that Watts obtained no evidence of absorption on forty-eight hours soaking. The writer's experience is that no ware not carried beyond normal vitrification is without open pores. It is also his experience that vitrified ware which shows no appreciable absorption in forty-eight hours ordinary soaking will show as high as 2% or more porosity when saturated in a vacuum. Owing to the apparent discrepancy in the apparent specific gravity, no further discussion of these results other than that the strength of the porcelains shows deterioration with increase in volume of sealed voids would be warranted.

CONCLUSIONS.

The following have been made evident:

(1) That porcelains, and the same is true of other vitrified wares, are not the solid masses that we have been led to believe they were by the customary absorption, porosity and shrinkage measurements.

(2) That in some cases there is unquestioned molecular volume alteration.

(3) That whether the sealed voids are the original open pores sealed off or new pores developed by formation and expansion of inclosed gases has not been made plain in these studies. Whatever may be the causes for the increase in volume of the solid material and the sealed pores it remains that these increases are considerable.

(4) That the strength of the porcelains so far as can be judged by these unsatisfactory data seem to be dependent upon the amount of sealed pores.

(5) That the data does not warrant making any statements regarding the effect of molecular increase in volume of the solid portion on strength of porcelain.

THE INFLUENCE OF FLUXES AND NON-FLUXES UPON THE CHANGE IN THE POROSITY AND THE SPECIFIC GRAVITY OF SOME CLAYS.

BY

A. V. Bleininger and J. K. Moore, Champaign, Ill.

Vitrification may be said to be partial fusion. When speaking of clays the progress of vitrification is equivalent to progressive, partial fusion of the various mineral constituents, governed by the mineral constitution of the body as a whole, the size of grain and the structure of the ware for which the clay is employed. Complete vitrification ensues when enough clay has been used to fill up the pores originally present. From the practical standpoint this is indicated by the fact that but little water is absorbed by the clay on immersion. Without going fully into the details of the process it may be said that the phenomena of fusion accompany the vitrification of clays.

Fusion considered from the general standpoint of silicates is sharply defined only for some definite minerals; even in many silicates it is a more or less gradual transition from the solid to the semi-liquid or liquid condition, and therefore, in a heterogeneous rock, like clay, even though all of its constituents were reduced to uniform, extreme fineness, fusion must, in the nature of the case, cover a considerable temperature interval.

From the practical standpoint, therefore, vitrification may be followed by determining the porosities at different temperatures, just as Prof. Purdy has done in his valuable contribution in Vol. IX of the Transactions of this Society.

In addition, two phenomena of fusion demand our attention. These are closely related and are: Change in molecular volume and transference of heat. In nearly all silicates the volume is increased on fusion or, in other

words, the density is decreased. This increase in volume is intimately connected with the fact that the amorphous or fused condition represents a greater energy potential than the crystalline state. We find, as a rule, that the amorphous modification of a substance is more soluble and capable of stronger reaction than the anisotropic form. That fusion results in an increased volume has been determined frequently, and in a few cases it was even possible to establish this fact for minerals in the fused, liquid condition. Thus Doelter found the specific gravity of crystalline augite to be 3.3, that of the hot, liquid mass 2.92, and of the solidified glass, 2.92. The so-called coefficient of crystallization, in fact, is determined by the specific gravity of an intermediate stage compared with the specific gravity of the crystal. If d_x=specific gravity at any stage and d_c=specific gravity of the crystal, $d_x \div d_c$=coefficient of crystallization. E. V. Fedorow has shown that this agrees with the facts.

With reference to the heat of fusion we can say that this is of constant magnitude, and is equal to about 100 gram calories per gram. Fusion is always accompanied by absorption of heat. This is a necessary conclusion, for in fusion, work is always done against the external pressure and the cohesion of the particles, both of which tend to oppose the increase in volume. That the non-crystalline condition corresponds to a higher level of energy may be indirectly shown by experiments such as the determination of the heat of solution. Thus 1 gram of crystalline sodium silicate evolves 457 calories, while the same amorphous substance gives off 486 calories. Similarly, crystalline leucite shows 507, the amorphous substance 533 calories.

From what has been said it follows that crystallization shows the opposite characteristics. On crystallization the volume decreases and heat is given off, thus retarding the cooling of the mass.

The fact that clay bodies decrease in density on vitrification had been realized quite early by Laurent, Brongniart and Rose, and during the last decade has been used

in very exact work by Day and Shepherd, Mellor and others. The rate of change in specific gravity and porosity has been employed in the plotting of density and porosity curves by Berdel in his excellent and extensive work on white ware bodies and, later, by Purdy in his work already cited. Purdy emphasizes the rate of change in porosity and makes use of the specific gravity only for the purpose of determining the porosity which he considers as the criterion for judging the progress of vitrification. He calculates the porosity, expressed in per cent, from clay brickettes burnt at different temperatures and uses the formula:

$$\% \ P = \left(\frac{W - D}{W - S}\right) 100,$$

where % P=per cent porosity.
W=wet weight of brickette.
D=dry weight.
S=suspended weight.

The wet weight corresponds to the weight of the brickette after immersion in water, in vacuo.

By plotting the porosities of a clay at different temperatures he obtains a curve which unquestionably indicates the progress and rate of vitrification. Prof. Purdy advocates the use of such curves in clay testing for the purpose of determining the character of a clay, and there is no doubt but that this offers a very convenient and valuable method of testing which deserves general application. The writers make continuous use of the method in carrying on clay tests.

While the porosity curve is of great practical value, yet it seems to the writers that much information in regard to the mechanism of the changes occurring in clay during burning is obtained from the particular study of the changes in specific gravity, that is, the specific gravity curves. In using this method we are simply adopting the means employed by many investigators in following chemi-

cal transformation, as, for instance, by Van't Hoff in his study of plasters, etc.

While in many clays and clay bodies the porosity and specific gravity curves are practically parallel, yet it may happen that certain changes occur which are indicated only by the specific gravity curve.

In discussing the density of clays we must clearly distinguish two values of the density which differ according to the method by which the work is carried out. If we take a brickette, weigh it when dry, immerse it in water, in vacuo, and again weigh it suspended in water, we obtain by calculation from the simple formula:

$$\text{Specific gravity} = \frac{\text{Dry weight in air}}{\text{Dry weight in air—suspended weight,}}$$

the specific gravity of the brickette as a whole, including the effect of enclosed pores and other cavities. On the other hand, by crushing and powdering the brickette and using the pycnometer, being careful to exhaust the air from the powdered material and water in the apparatus, we shall have the specific gravity of the burnt clay itself, the effect of the pores and cavities having been eliminated.

In addition to the change in volume brought about by fusion we have other volume transformations caused by so-called inversions, that is, the character of the molecular arrangement of many compounds suffers an alteration. The best known instance of this kind of transformation is the change of quartz into tridymite. On filling a crucible with pulverized quartz and heating it this change is manifested quite strikingly by the bursting of the vessel due to the increase in volume incident to this molecular change. This inversion

$$\text{quartz} \rightleftarrows \text{tridymite}$$

occurs at about 800°C. Similarly it is found that fused quartz which necessarily is in the amorphous condition is transformed to tridymite, which is shown by the dim-

ming of the glass. Since this change is reversible it follows that below 800° the tridymite reverts to quartz. This latter change is rather sluggish and requires considerable time, we can say, therefore, that quartz never crystallizes from mineral fusions excepting in the presence of catalyzers. Quartz* then, is the unstable form of silica from 800° upward, and it will change to tridymite whenever opportunity offers. We have thus a volume change which on heating a clay is shown by the decrease in density. Purified natural quartz has a specific gravity of 2.654 (25°), while tridymite prepared from quartz has a density of 2.326; when prepared from fused quartz its density is 2.318. The density of quartz glass was found to be 2.213. On cooling a clay any change from tridymite to quartz stands for an increase in density, as must be evident from the above figures.

Similar inversions are known for meta and ortho calcium silicate. Thus we have the pseudo-hexagonal metasilicate and wollastonite and three forms of the ortho calcium silicate. These are the alpha, beta and gamma modifications whose densities are 3.27, 4.28, and 2.97, respectively. There are doubtless other inversions which are not yet known to us.

Still another source of volume changes is to be sought in chemical reactions taking place in clay, such as the exothermic reaction taking place in clay substance at about 1000°, in which evidently an isomeric compound differing from the previous composition in structure is formed. Other examples are the chaneg of calcium carbonate to the oxide, the interaction of lime and iron oxide, the formation of certain lime silicates above 1200°, the formation of spinels, magnetic oxide, etc. There must be many chemical reactions which at present are entirely unknown to us.

In studying the changes in the two specific gravities, then, we might be able to summarize the causes of the volume changes as follows:

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*Day and Shepherd. Jour. Am. Chem. Soc., Vol. 28, p. 1099.

A. Apparent specific gravity.

1. Inversion
2. Fusion
3. Chemical reactions
4. Pore space
5. Formation of "blebs"
6. Crystallization.

B. True specific gravity.

1. Inversion
2. Fusion
3. Chemical reactions
4. Crystallization

A slight change common to both forms of specific gravity is that caused by the differences in the coefficient of expansion between the fused and crystalline portions. We observe, hence,, that the apparent specific gravity must be the algebraic sum of at least six and thee true specific gravity of four factors.

On heating a clay body the changes taking place in quartz and feldspar and perhaps in clay substance, the character of which has been discussed before, tend to increase the volume or to decrease the density. We might say, therefore, that, in terms of the density, the change is— in character. On cooling the clay, however, during the critical temperature intervals of each constituent inversed, the density change is+for then the inversion, as far as reversible, proceeds the other way. But since the cooling nearly always takes place far more rapidly than the heating up, it is quite probable that this change in volume is but slight.

We already know that the volume is increased on fusion and remains increased unless crystallization takes place on cooling. The change in density on fusion, hence, is—as far as most silicates are concerned.

Chemical reactions may cause either + or — changes, but on heating, according to the theorem of Le Chatelier, the changes are probably — in sign, as a rule.

The pore space, still remaining in the clay which has not yet been closed up by the softened or fused material of course, tends to decrease the apparent density. The same thing is true of the blebs formed by the evolution of

gases within the clay. This formation of gas is a very important factor in the mechanical strength developed in a clay, and this fact has been brought out very clearly by Purdy. In some clays the porosity thus contributed may be coincident with vitrification and hence, although the clay itself may be perfectly vitrified, the porosity curve would, in such a case, fail to indicate vitrification. Several such clays and bodies have been observed by the writers.

Crystallization would, in the nature of the case, take place only when the temperature has ceased to rise, that is, when the kiln is "soaking," the temperature just holding its own or when cooling begins.

That crystallization does take place to some extent in clays is established beyond a doubt. The senior writer in examining a section of paving brick which happened to show two well defined areas of properly burnt and over-burnt clay, found numerous crystals, needle-like in shape, in the over-burnt portion, but no evidence of crystallization in the sound part. Wegemann, in collaboration with Prof. Purdy, found considerable crystallization in over-burnt paving brick, fine needle-like crystals, yellowish-green in color, of unknown composition as well as minute crystals of iron oxide. Crystallization, as we know, stands for decrease in volume or increase in density, and hence we may say that it is a + change, in terms of the density.

The investigation which is the basis of this paper was carried on for the purpose of determining the character of the changes in the density and porosity of clay bodies to which various reagents have been added, burnt at different temperatures, and it is due Prof. Purdy to say that it was inspired by his paper on the pyrochemical and physical changes of clays. It was proposed to broaden the scope of the work and to determine, if possible, the following questions:

1. To what extent do the apparent specific gravity and porosity curves agree in indicating vitrification in the study of various additions to clays?

2. If there are any deviations where and how do they

occur, and what is their character? Are there any maximum or minimum points?

3. Under what conditions are certain substances fluxes, and when are they non-fluxes or refractories?

4. At what rate do these substances either accelerate or retard fusion?

5. At what temperatures does the fluxing or refractory character of certain additions begin?

6. What are the areas enclosed by some isothermals?

In the work of Purdy the specific gravity and porosity curves agree quite well in indicating vitrification, and hence it is but natural to inquire whether this is the case under all conditions. Any deviations might be reasonably ascribed to conditions pointing towards certain physical or chemical phenomena peculiar to the composition studied, since we know that the density changes with the transformation caused by chemical reactions, solution or crystallization.

The term flux is but a relative one, and no particular class of substances can be designated as fluxes. In a silicious material like clay, basic substances act as fluxes, while in basic compositions like Portland cement silicious compounds unquestionably behave as such. In addition we must consider the fact that a small portion of any substance, no matter what its composition, dissolved in another, will lower the fusing point, provided no chemical reaction takes place.

The rate of these changes is of interest in as much as this factor may have considerable influence upon the practical application. It may be either too rapid or too sluggish. In this manner we can establish the point at which no further change is observed and when additional amounts show no effect.

The question of temperature establishes the points at which the activity of the various additions become manifest and at what temperature the maximum effect is shown.

The areas enclosed by successive isothermal curves are designed to show the rate at which vitrification progresses,

and the composition of the fusible combination as well as the change in the composition on raising the temperature. It might be said that thus the changes in the eutectic combinations are indicated.

The clays upon which the effect of various substances was studied were as follows:

1. Florida kaolin, and in several instances, Georgia kaolin.
2. Ball clay, Tennessee No. 3.
3. Shale from Galesburg, Ill.
4. Shale from Crawfordsville, Ind.
5. Shale from Canton, Ohio.

The materials added to the above clays were as follows:

1. Feldspar
2. Whiting
3. Ferric oxide
4. Flint
5. Florida kaolin
6. Feldspar-flint
7. Whiting-flint
8. Ferric oxide-flint
9. Ferric oxide-whiting
10. Cornish stone

The composition of some of the materials are given in the following table:

	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	FeO %	TiO_2 %	CaO %	MgO %	K_2O %	Na_2O %	Loss on ignition. %	Moisture %
Galesburg* Shale	63.62	16.31	6.22	2.88	0.96	0.63	1.44	2.60	1.50	6.26	0.38
Crawfordsville* Shale	68.50	16.98	5.77	....	....	0.99	1.71	2.97		7.33	0.27
Canton* Shale	55.51	22.21	7.26	....	....	0.56	1.63	3.56		8.00	....
Feldspar	68.22	17.83	.....	....	....	0.30	0.11	12.13	1.90	0.35	....
Flint	98.00	.....	.....	....	....	.....	....	.....	....	....	....
Iron Oxide	.....	.....	99.00	....	....	.....	....	.....	....	....	....
Whiting	1.62	3.50	.....	....	....	52.65	....	.....	....	....	0.50

*Purdy and Moore, Trans. Am. Cer. Soc., Vol. 9.

The compositions are expressed in percentages throughout, since the changes to be noted are shown in this manner as well as if molecular relations had been employed. In fact, considering the heterogeneous character of the clays used and their physical differences, the consideration of chemical formula would have appeared to be almost absurd. This is especially true since we were dealing only with the vitrification and not the fusion of bodies, and particularly since the earlier stages of vitrification were of special interest to us.

The materials were weighed out in the dry condition, and usually the two ends of a series were ground dry in the ball mill for two hours. From the two end compositions the intermediate mixtures were obtained by blending and thorough grinding in a mortar. Each batch was then made up with water to the desired consistency, and after thorough wedging was molded into a brickette of the dimensions: 12.8x7.8x1.3 cm. in a brass mold provided with a movable bottom. Each brickette was cut up into eight prisms, which were stamped with the series numbers. After thorough drying one brickette from each mixture was taken and placed in a sagger. Each burn, therefore, contained one of the eight small brickettes of every composition. The saggers were placed and cones put in the kiln, well protected from any direct flame. The kiln used was a down-draft test kiln, fired with coke, and has been described in the paper on "Fritted Glazes" by R. C. Purdy and H. B. Fox.* The firing temperatures were cones 09, 06, 03, 01, 2, 4, 6; some brickettes which had been left by Prof. Purdy as part of an unfinished investigation were fired to cones 9, 11, and 13. The cooling of the kiln was hastened in no case, though the damper was left open.

The brickettes when cold were freed from adhering particles, weighed, and immersed in distilled water for 48 hours; they were then boiled for one hour and finally placed in a large suction flask connected to a filter pump

*Trans. Am. Cer. Soc., Vol. IX.

and left there until no more air bubbles were given off, which usually took several hours. This method was found to be more satisfactory than exhaustion by an air pump, as it seemed to result in better absorption of water. The brickettes were then suspended in water by attaching with a silk thread to the beam of the balance and thus weighed. Immediately afterwards they were weighed in air, thus giving the wet weight. The specific gravity was calculated by the usual formula and the porosity by the Purdy formula.

Several hundred pycnometer specific gravity determinations were also made on the dried and pulverized brickettes by weighing a quantity of the powder in the pycnometer and filling the pycnometer a little more than half full of warm water. The pycnometer was then attached to a bent 50 cc. pipette, which contained some water. The other end of the pipette was connected to the filter pump and the air exhausted from the powder. The vacuum was sufficient to cause the water in the pycnometer to boil at a temperature of about 30°. After no more air bubbles were evolved the pycnometer was filled by raising the pipette and allowing the air-free water to run into the apparatus. In making these determinations special pains were taken to dry the powder in an air bath at a temperature never less than 120°. Some of the pycnometers were collapsed by the air pressure.

Comparing the specific gravities by the two methods the differences are shown to be of the following order of magnitude:

Spec. gr. pycnom.	2.69	2.62	2.73	2.76	2.65	2.66	2.67	....	....
Spec. gr. suspension	2.55	2.51	2.54	2.56	2.57	2.58	2.61	....	....
Difference	0.14	0.11	0.19	0.20	0.08	0.08	0.06	....	....
Spec. gr. pycnom.	2.68	2.65	2.65	2.64	2.64	2.67	2.67	....	....
Spec. gr. suspension	2.62	2.61	2.59	2.61	2.57	2.63	2.59	....	....
Difference	0.06	0.04	0.06	0.03	0.07	0.04	0.08	....	....
Spec. gr. pycnom.	2.66	2.65	2.67	2.64	2.64	2.64	2.67	....	....
Spec. gr. suspension	5.56	2.61	2.61	2.62	2.61	2.58	2.59	....	....
Difference	0.10	0.04	0.06	0.02	0.03	0.06	0.08	....	....
Spec. gr. pycnom.	2.65	2.67	2.66	2.70	2.67	2.70	2.67	2.68	....
Spec. gr. suspension	2.60	2.61	2.60	2.59	2.60	2.68	2.66	2.64	....
Difference	0.05	0.06	0.06	0.11	0.07	0.02	0.01	0.04	....
Spec. gr. pycnom.	2.70	2.65	2.67	2.70	2.71	2.78	2.73	2.72	2.59
Spec. gr. suspension	2.62	2.62	2.61	2.66	2.60	2.80	2.58	2.69	2.51
Difference	0.08	0.03	0.06	0.04	0.11	0.07	0.15	0.03	0.08

The sensibility of weighing in the pycnometer experiments was about 0.5 milligram for one balance and 1 milligram for another, the average sample of powdered material averaging 8 grams. The error of weighing thus varies from 0.005 to 0.01 per cent. In the suspension method the weight of the brickettes varied from 15 to 20 grams. The sensibility of the balances was about 2 centigrams, which corresponds for the 15 gram brickette to a variation of 0.13 per cent.

From these results it is clearly seen that the specific gravity determinations by suspension are greatly affected by the porous structure of the clay, that is, by the pores into which water cannot penetrate. It was recognized that in order to obtain comparable specific gravity curves the true specific gravity would have to be used. But since these determinations consume much more time, and the main aim of the experiments planned was chiefly a practical one, it was decided to use only the apparent specific gravities and porosities in obtaining the rates of vitrification, since after all it is the *rate* and not the absolute values that interested the writers most at the time. The study of the true specific gravities has been reserved

for mixtures whose components have themselves been defined more closely by chemical and physical methods, and which are intended to be simple mixtures rather than such complex ones as are afforded by the shales. By this method it was possible to cover the ground more rapidly, and about 4000 determinations were made. Owing to this large mass of data it is impossible to reproduce all of the rate curves thus obtained, and hence only the typical cases are presented.

We shall now discuss the additions of the various reagents to the clays mentioned above.

FELDSPAR.

Feldspars are considered neutral body fluxes. By this is meant that their fluxing effect is additive, they being simply solvents of the clay substance and the free silica. Feldspar naturally lowers the melting point of a body most when it is added to the eutectic combination of kaolin and quartz, which corresponds to the ratio of 1 : 3. This is shown very clearly in the clever work of Dr. M. Simonis* on "Tme Fusion Points of Mixtures of Zettlitz Kaolin, Quartz and Feldspar Expressed in Cones."

By means of a simple arithmetical expression, for which he claims no theoretical or scientific significance, though he suggests its practical use, he calculates the refractory quotient for bodies high in clay and high in quartz. In the first case, that is, in clayey bodies in which the per cent of kaolin is greater than one-third of the per cent of quartz, or where $K > \frac{qu}{3}$ Simonis obtains his refractory quotient by the formula

$$R.\ F. = K - \frac{qu}{3} - f + 60,$$

where K = % kaolin
qu = % quartz
f = % feldspar.

*Sprechsaal, Vol. 40, Nos. 29 and 30.

For silicious bodies in which

$$K < \frac{qu}{3}$$

the formula employe is:

$$R.\ F. = \frac{\frac{qu}{3} - K}{2} - f + 60.$$

The number 60 is added to prevent negative values. The values of the refractory quotient are translated into cone temperatures by the following table:

Refractory quotient	17.5	22.6	28.0	33.7	39.2	44.6	50.0	57.6
Melting point in cones.....	14.0	15.0	16.0	17.0	18.0	19.0	20.0	26.0
Refractory quotient	65.0	72.0	80.0	89.0	102.0	114.0	127.0	141.0
Melting point in cones.....	27.0	28.0	29.0	30.0	31.0	32.0	33.0	34.0

From the consideration of the Simonis calculation it is evident that feldspar plays the role of a neutral flux.

With regard to the fusion process of triclinic feldspars we have accurate data referring to artificial spars,* which had the following composition:

	An	Ab_1An_5	Ab_1An_2	Ab_2An_1
SiO_2	43.33	47.10	51.06	60.01
Al_2O_3	36.21	34.23	31.50	24.95
Fe_2O_3	0.29	0.15	0.22	0.29
CaO	20.06	17.00	13.65	7.09
Na_2O	0.11	1.74	3.68	7.79

We have here evidently mixtures of albite and anorthite, and on fusing a series of these mixtures it was found that they proved to be a series of solid solutions whose

*Day and Allen. The Isomorphism and Thermal Properties of the Feldspars, Carnegie Inst., 1905.

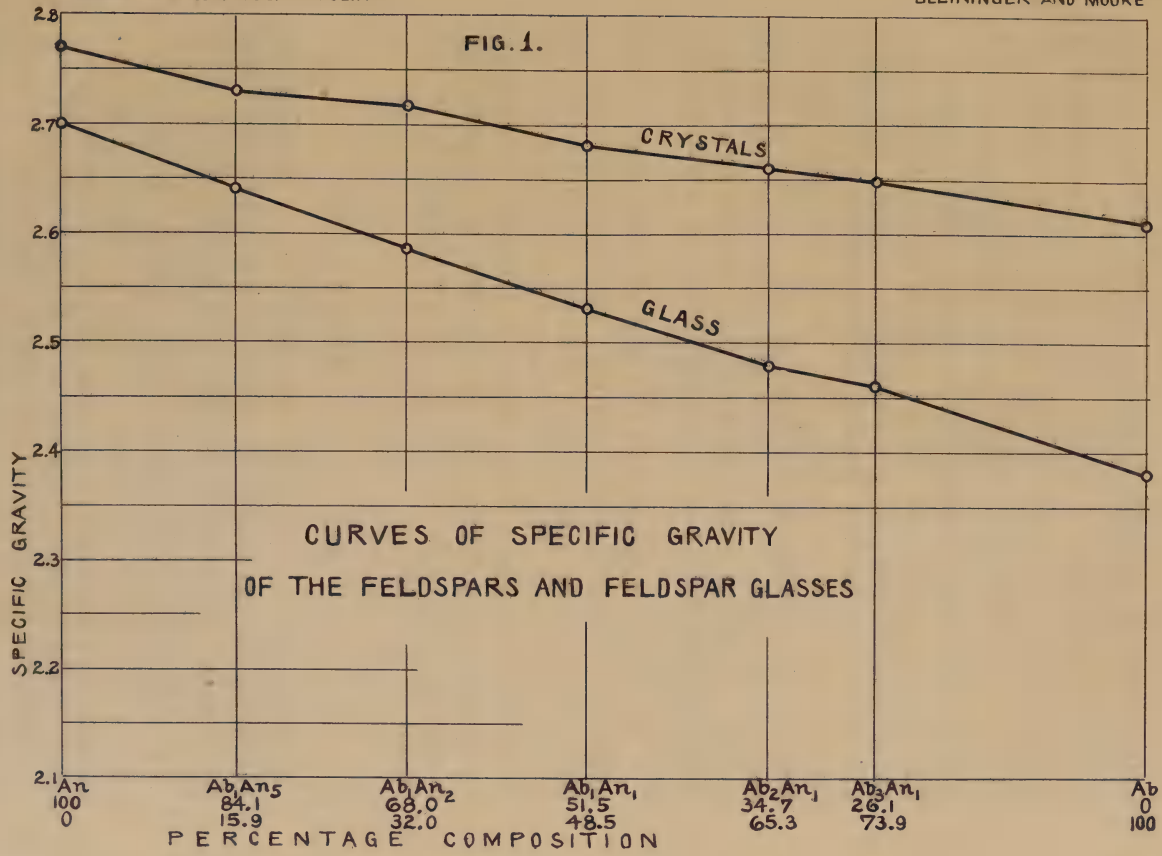


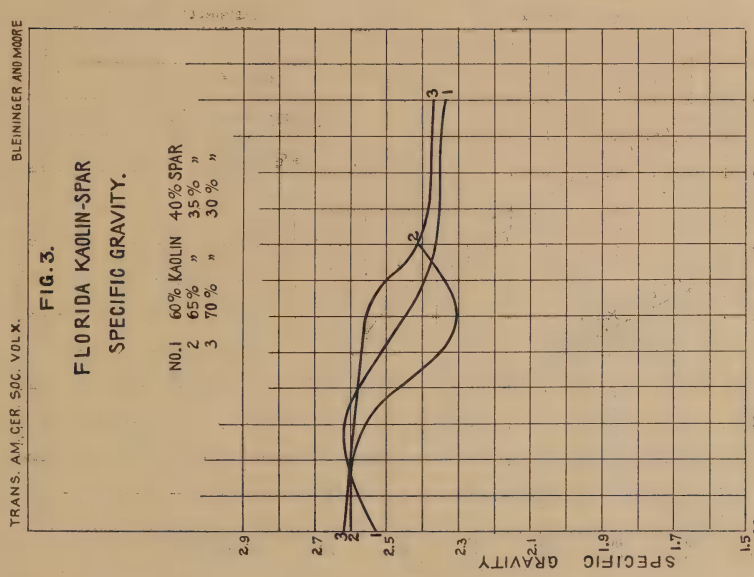
FIG. 1.
CRYSTALS
GLASS
CURVES OF SPECIFIC GRAVITY
OF THE FELDSPARS AND FELDSPAR GLASSES
SPECIFIC GRAVITY
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
An 100 0
Ab1An5 84.1 15.9
Ab1An2 68.0 32.0
Ab1An1 51.5 48.5
Ab2An1 34.7 65.3
Ab3An1 26.1 73.9
Ab 0 100
PERCENTAGE COMPOSITION

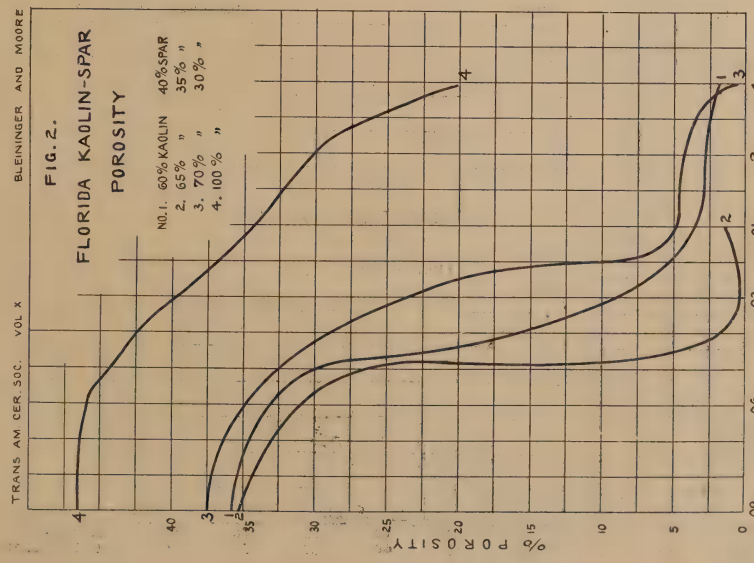
melting points changed in almost linear relation to the percentage composition of the two silicates. From this result Day and Allen conclude that the triclinic feldspars "form together an isomorphous series." This relation is brought out clearly by the curve of Fig. 1, in which the rate of change in the specific gravity of mixtures between the anorthite and albite is shown to be a linear relation. This tends to show that we are dealing here with isomorphous mixtures and at the same time explains why they have no definite melting points. Albite was proven to melt through a range of about 150°. Although the melting point of the average feldspar as used in the industries is about at cone 8, yet its interaction with clay substance begins at a much lower temperature. Berdel found that the dissolving action of orthoclase feldspar began as low as cone 09.

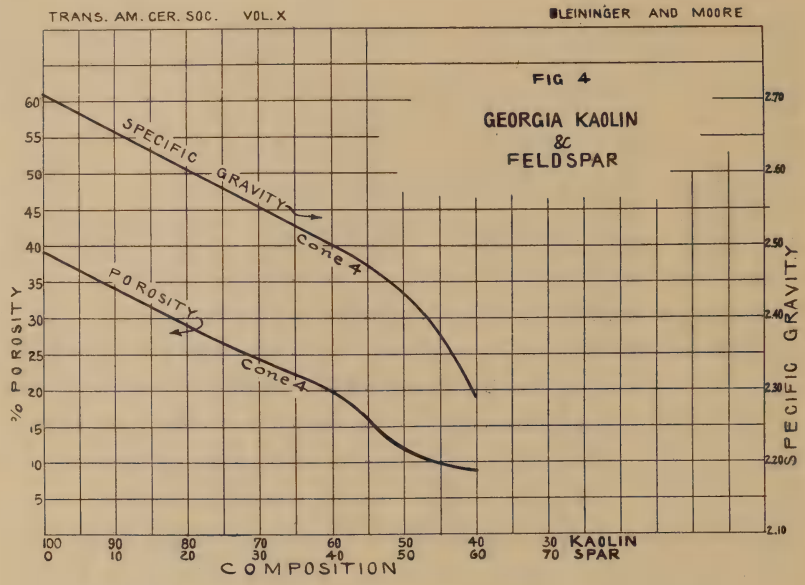
On fusing mixtures of the trilinic feldspars it was found that their melting points were connected by a straight line, the same linear relation that held for the specific gravities. This shows likewise that the fusion of the triclinic feldspars is a continuous smoothly proceeding process, and it is even possible to calculate the composition of each point on the curve from the specific gravity or the fusion temperature.

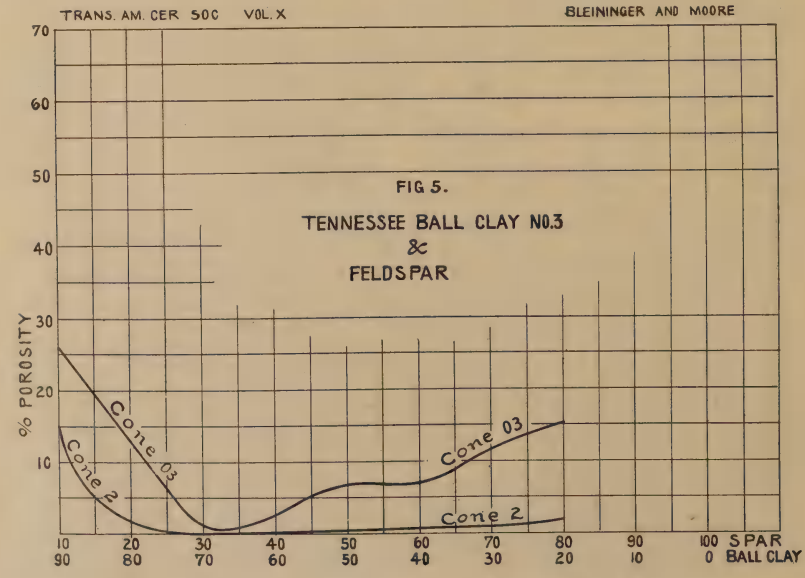
ADDITION OF FELDSPAR.

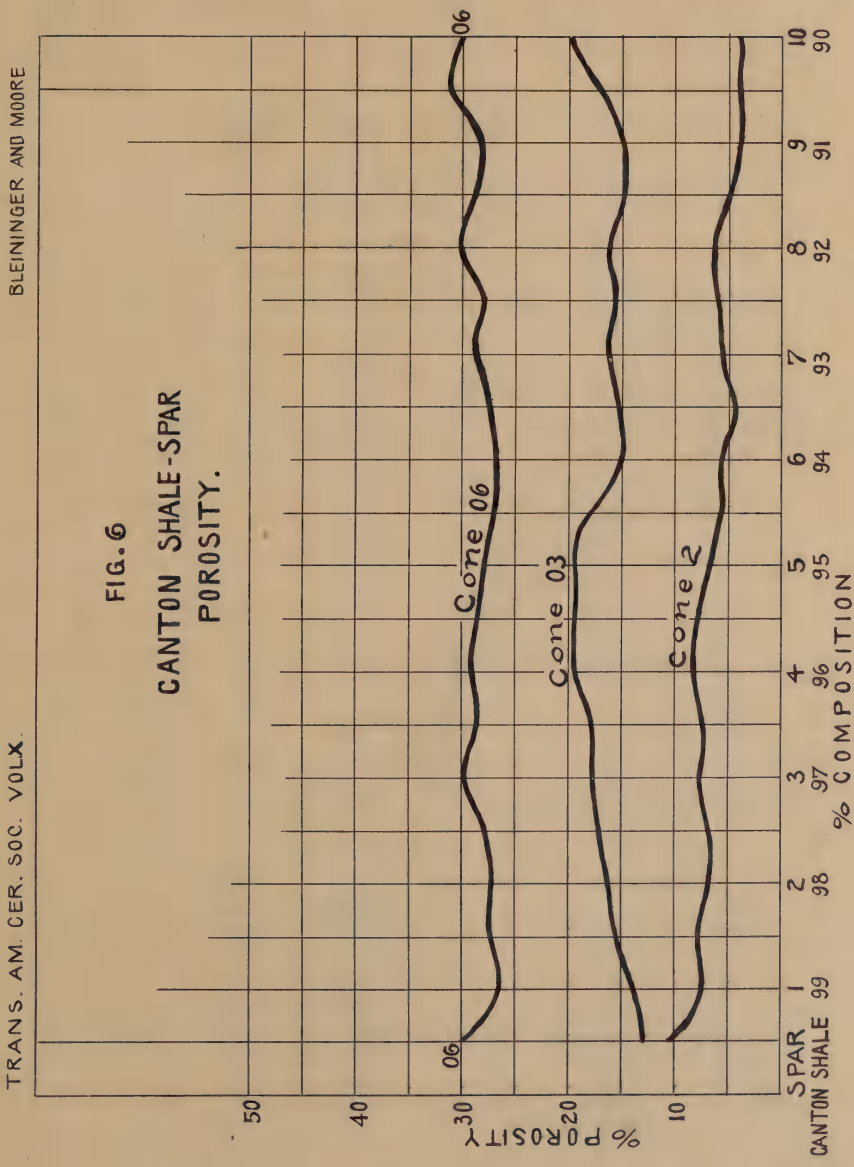
The behavior of orthoclase feldspar is shown sufficiently in the porosity and specific gravity curves of Figs. 2, 3 and 4. We observe that the vitrification due to feldspar is indicated both by the drop in the specific gravity and the decrease in porosity. We also find confirmed that the solution effect of feldspar begins at quite a low temperature, at least as low as cone 06. It is likewise shown quite distinctly that feldspar is a neutral flux and does not undergo any chemical reactions. The only minimum is that due to the eutectic mixture which, however, was not fixed in these series. The solution of kaolin by feldspar


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG. 3.
FLORIDA KAOLIN-SPAR
SPECIFIC GRAVITY.
NO. 1 60% KAOLIN 40% SPAR
2 65% " 35% "
3 70% " 30% "
SPECIFIC GRAVITY
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
09
06
03
01
2
4
CONES


TRANS AM CER. SOC. VOL X
BLEININGER AND MOORE
FIG. 2.
FLORIDA KAOLIN-SPAR
POROSITY
NO. 1. 60% KAOLIN 40% SPAR
2. 65% " 35% "
3. 70% " 30% "
4. 100 % "
% POROSITY
40
35
30
25
20
15
10
5
0
09
06
03
01
2
4
CONES


TRANS. AM. CER. SOC. VOL. X
BLEININGER AND MOORE
FIG 4
GEORGIA KAOLIN
&
FELDSPAR
SPECIFIC GRAVITY
Cone 4
POROSITY
Cone 4
% POROSITY
SPECIFIC GRAVITY
60
55
50
45
40
35
30
25
20
15
10
5
2.70
2.60
2.50
2.40
2.30
2.20
2.10
100 0
90 10
80 20
70 30
60 40
50 50
40 60
30 70
KAOLIN
SPAR
COMPOSITION


TRANS. AM. CER SOC VOL. X
BLEININGER AND MOORE
FIG 5.
TENNESSEE BALL CLAY NO.3
&
FELDSPAR
% POROSITY
70
60
50
40
30
20
10
Cone 03
Cone 2
Cone 03
Cone 2
10 90
20 80
30 70
40 60
50 50
60 40
70 30
80 20
90 10
100 0
SPAR
BALL CLAY


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG. 6
CANTON SHALE-SPAR
POROSITY.
% POROSITY
50
40
30
20
10
06
Cone 06
Cone 03
Cone 2
SPAR 1 2 3 4 5 6 7 8 9 10
CANTON SHALE 99 98 97 96 95 94 93 92 91 90
% COMPOSITION

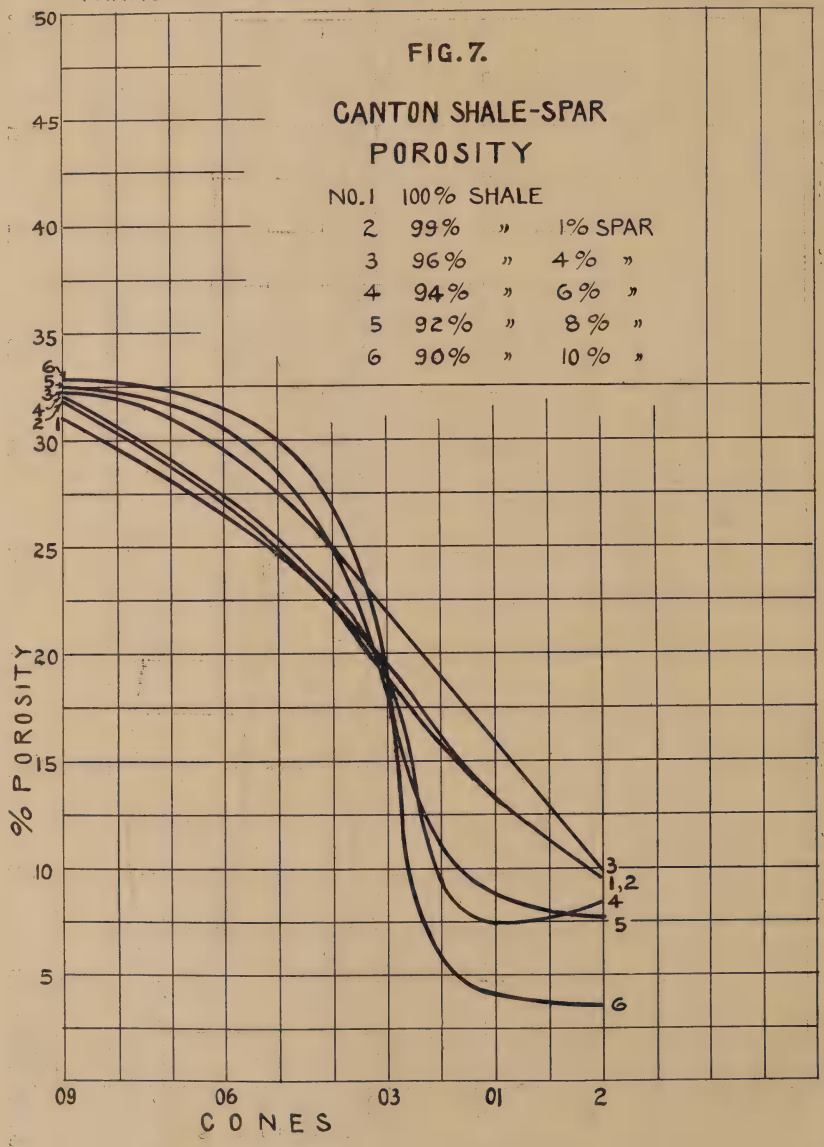


FIG. 7.
CANTON SHALE-SPAR
POROSITY
NO. 1 100% SHALE
2 99% " 1% SPAR
3 96% " 4% "
4 94% " 6% "
5 92% " 8% "
6 90% " 10% "
% POROSITY
50
45
40
35
30
25
20
15
10
5
09
06
03
01
2
CONES
1
2
3
4
5
6
1,2

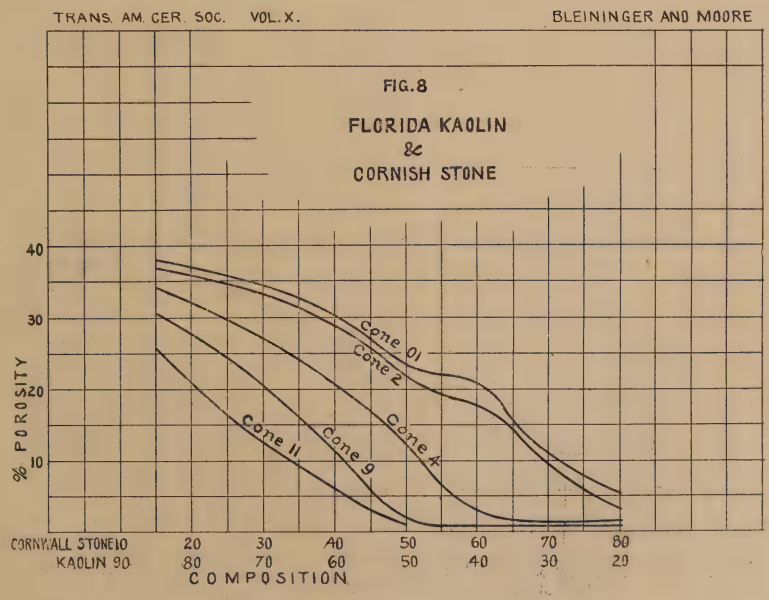
takes place at a fairly rapid rate, which shows simply that there seems to be no physical obstacle to this mutual solution.

The curves also bring out the difference in the behavior of Georgia kaolin and Florida kaolin.

In Fig. 5 we have the porosity curve of mixtures of Tennessee ball clay No. 3 with feldspar, and it is evident that feldspar in this case becomes far more potent in its action than in the cases of the two kaolins.

The effect of various percentages of feldspar upon Canton shale is shown in Fig. 6, and we observe that though the first additions cause a small decrease in porosity, the result shows practically no gain in fusibility or vitrification. The same fact is brought in Fig. 7, in which some of the shale-spar curves are arranged.

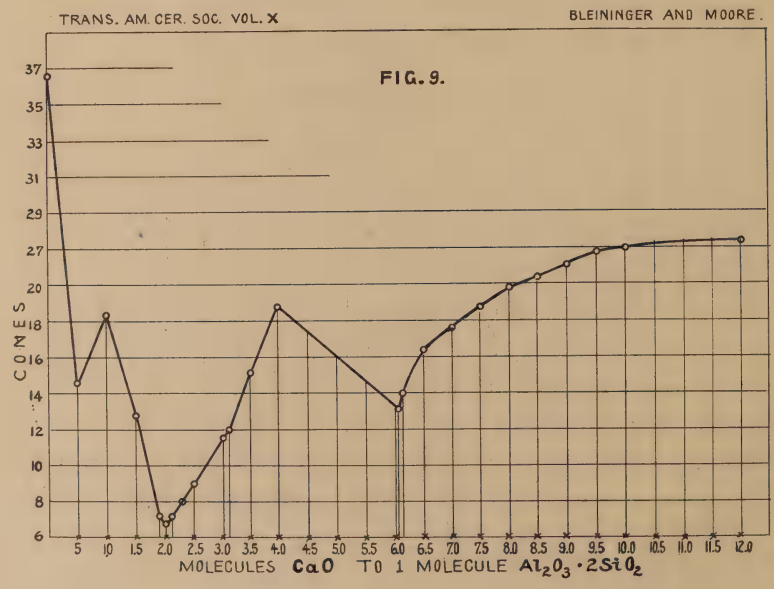
In this connection it was also interesting to observe the action of Cornish stone on kaolin as shown by Fig. 8.



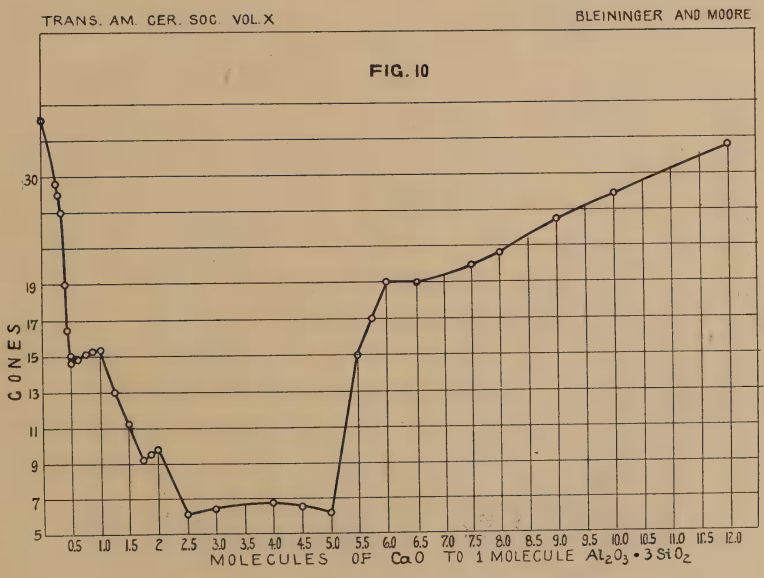
Here we note distinctly the slow, neutral fluxing effect of this material whose action is more gradual than that of the feldspar and which offers the safest flux, as far as range and rate of vitrification are concerned.

THE ADDITION OF LIME.

Kaolin and Ball Clay. In the addition of calcium carbonate to clays we are dealing with a flux which is unlike feldspar or Cornish stone. Its action is not gradual, but variable; that is, though its presence may not be observed by means of the porosity curve, at the proper reaction temperature it suddenly combines and causes as large an amount of fusible magma to be formed as is consistent with the composition of the body. At the same time there is to be considered the fact that lime-alumina-silica compounds form a number of maximum and minimum fusing compounds. This has been clearly shown in the work



of Rieke,* who investigated the melting points of mixtures of this kind in a most thorough and exhaustive piece of work, using an electric carbon resistance furnace for the determination of the melting points. We shall consider only his results, referring to the $Al_2O_3 : 2\ SiO_2$ mixtures and those higher in silica. The first curve brings out the fact already noted by Cramer† that for high temperatures, additions of CaO to kaolin, up to 10%, decrease the melting point in equal intervals. The lime-kaolin fusion curve of Rieke is reproduced in Fig. 9, the abscissa indicating the molecules of CaO to 1 molecule of $Al_2O_3 : 2\ SiO_2$, the ordinates the melting points in cones. With a content of 10% CaO we have a minimum corresponding to the formula CaO, .2 Al_2O_3, .4 SiO_2. On increasing the lime we find a maximum at the composition $CaO : Al_2O_3 : 2\ SiO_2$. With more lime the fusion curve descends again to a mini-



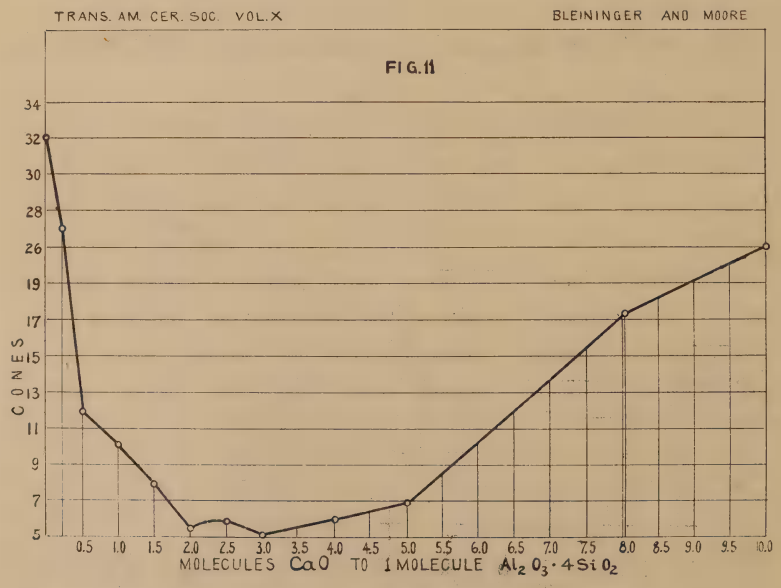
*Sprechsaal, Vol. 40, Nos. 44, 45, 46.

†Tonindustrie-Zeitung, 1887, p. 197, and 1888, p. 73.

mum 2 $CaO : Al_2O_3$ 2 SiO_2, which is the most fusible combination between kaolin and lime that exists corresponding to a percentage composition of 36.1% SiO_2, 30.5% Al_2O_3 and 33.4% CaO. On increasing the lime still more Rieke obtained a second maximum at 4 $CaO : Al_2O_3 : 2$ SiO.

This is followed by a third minimum 6 $CaO : Al_2O_3 :$ 2 SiO_2. After this it appears that no further decrease in melting point occurs. Since the maximum and minimum points very likely correspond to chemical combinations, it seems, according to Rieke, that there exist at least four distinct compounds of lime and kaolin.†

In the mixtures of CaO with $Al_2O_3 : 3$ SiO_2 shown in Fig. 10, there are observed four maxima and four minima which appear to show the existence of the following compounds and mixtures:



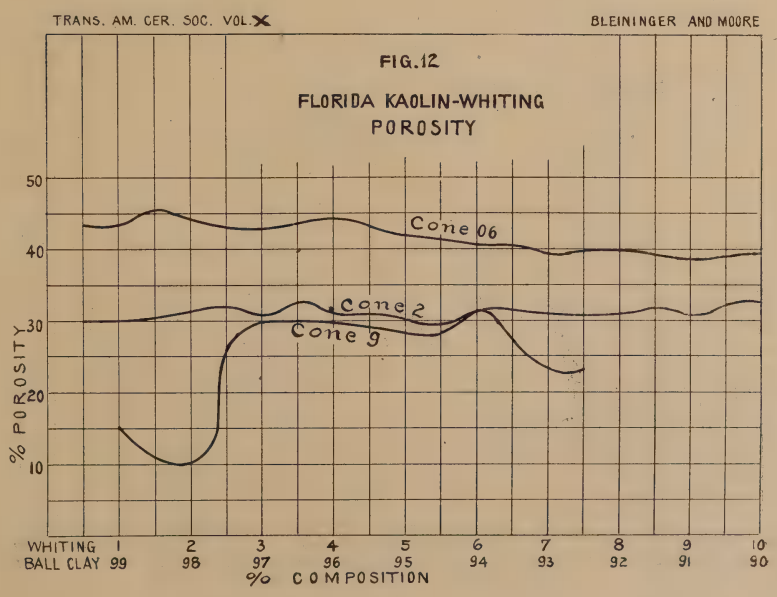
†Rieke's view that the minimum as well as the maximum points correspond to chemical compounds is open to criticism. The minimum points are probably eutectic mixtures.

	CaO	$2\ Al_2O_3$	$6\ SiO_2$		CaO	Al_2O_3	$3\ SiO_2$
7	CaO	$4\ Al_2O_3$	$12\ SiO_2$	2	CaO	Al_2O_3	$3\ SiO_2$
3	CaO	Al_2O_3	$3\ SiO_2$	4	CaO	Al_2O_3	$3\ SiO_2$
5	CaO	Al_2O_3	$3\ SiO_2$	6	CaO	Al_2O_3	$3\ SiO_2$
13	CaO	$2\ Al_2O_3$	$6\ SiO_2$				

Finally in mixtures of lime with Al_2O_3 and SiO_2 Rieke found one rather indistinct maximum, 5 CaO : 2 Al_2O_3 : 8 SiO_2 and two minima, Fig. 11. The curve as a whole is more regular than the preceding ones.

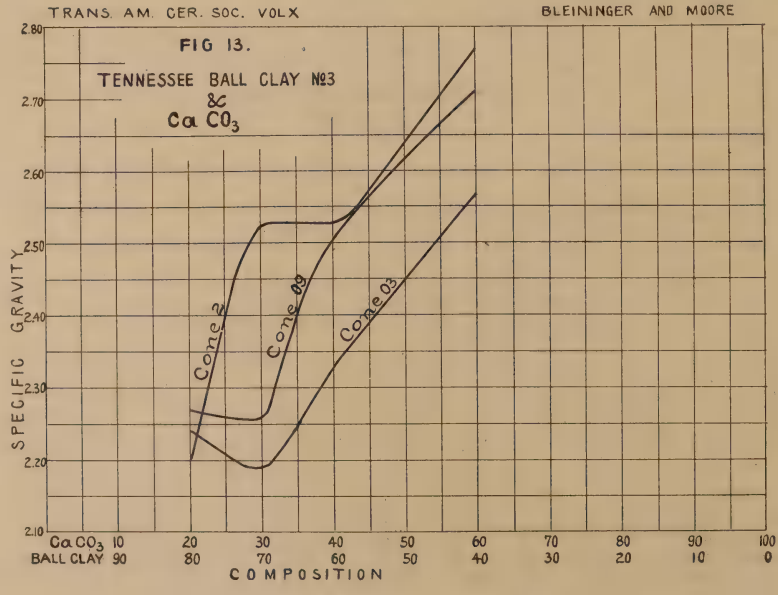
It is evident from these data that we cannot expect from lime-clay mixture the regularity of fusion induced by feldspathic fluxes, and it remains to be seen how the vitrification of different clays is affected by this flux.

Lime—Florida Kaolin Mixtures. Inspection of curve of Fig. 12 shows clearly that with increasing lime content at Cone 06 but little change occurs within the compositions examined, the mixture containing 10% whiting showing

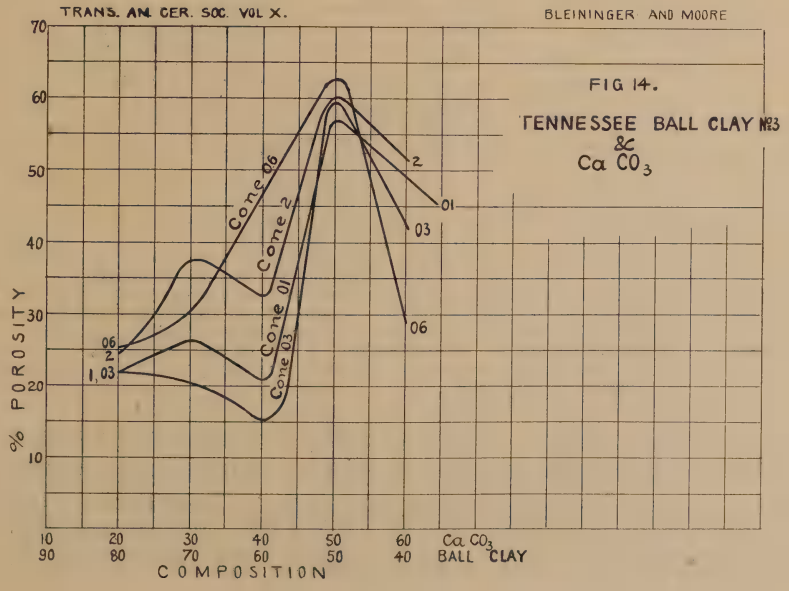


only 4% less porosity than the composition 99.5% kaolin, 0.5% whiting. We also observe that the first 2% of whiting in the Cone 9 curve are more effective in decreasing porosity than 3-6%, a second decrease in porosity taking place only beyond 6% whiting. Of course this is in agreement with the general theory of dilute solutions as suggested by Ludwig.

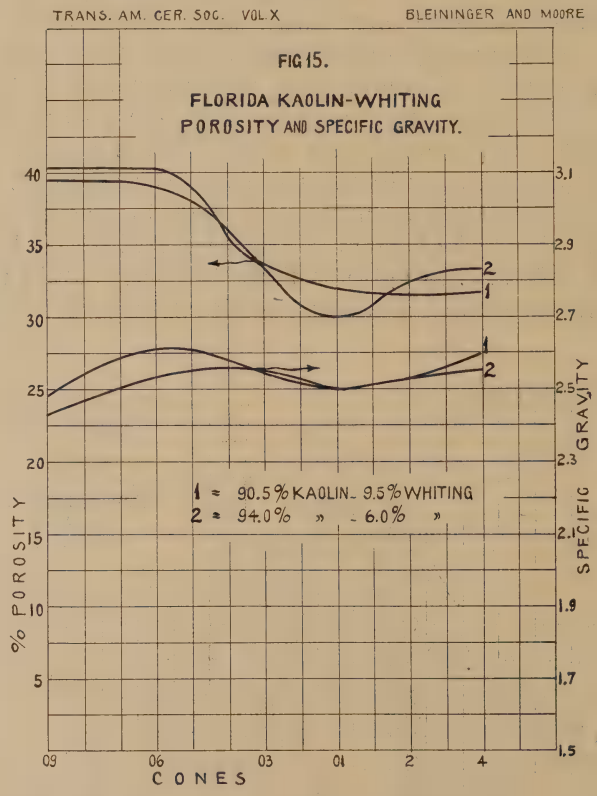
On studying mixtures of ball clay and larger amounts of lime we observe in the specific gravity curve, Fig. 13, a distinct minimum in the Cone 09, 03, and 2 burns at about 30% whiting and 70% ball clay, which corresponds roughly to the minimum $CaO : Al_2O_3 : 2\,SiO_2$ observed by Rieke. This seems to be the eutectic composition under these temperature conditions. The corresponding porosity curve, Fig. 14, shows two maxima and minima, the first maximum being at 30% whiting and 70% ball clay, the second at 50% clay, 50% whiting. The minimum is at 40% whiting, 60% ball clay, a second minimum is indicated, but not



reached. Of course it would be idle to claim that these maximum points actually do represent certain compounds, as we must remember that the apparent specific gravities are the resultants of a number of factors, of which not the least important is the temperature to which each brickette was raised in the kiln. It would be claiming too much to say that each brickette actually reached or did not exceed the temperature of the burn as indicated by the cone in each sagger. There must have been temperature differences. Another very important factor in the curves representing a series of compounds, is the constantly changing initial specific gravity of each mixture as we start from one side of the curve sheet to the other. For instance, the last series, on going from left to right increases in lime. Every increase in CaO thus means a change in specific gravity, and this should be borne in mind in examining subsequent curves. If, now, in spite of these factors, certain maxima and minima occur, coinciding, at least in most cases, with



similar points in the porosity curves, we are led to the conclusion that certain phenomena are taking place. The technical side of the vitrification progress is represented, of course, by the porosity curves. In Fig. 15 the action of 6 and 9.5% respectively of whiting is shown for the lower temperatures, and we observe that the decrease in porosity begins about between cones 06 and 01.

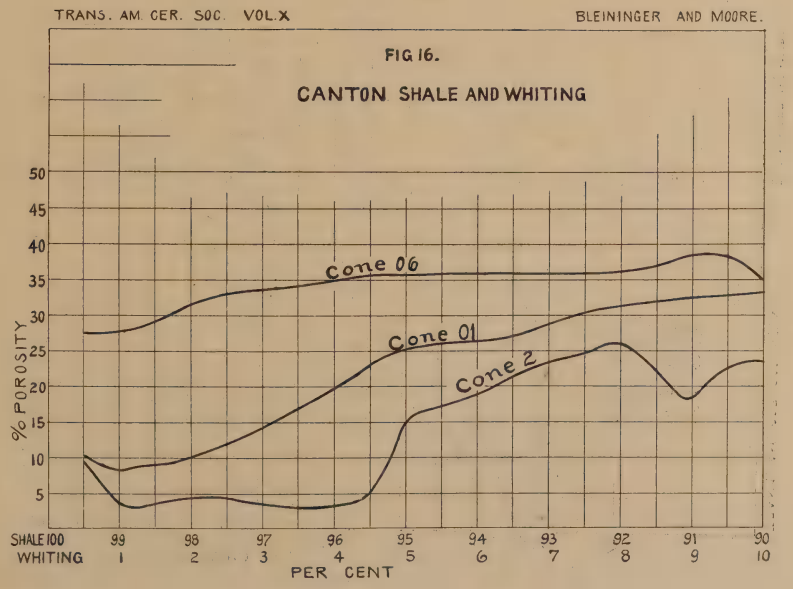


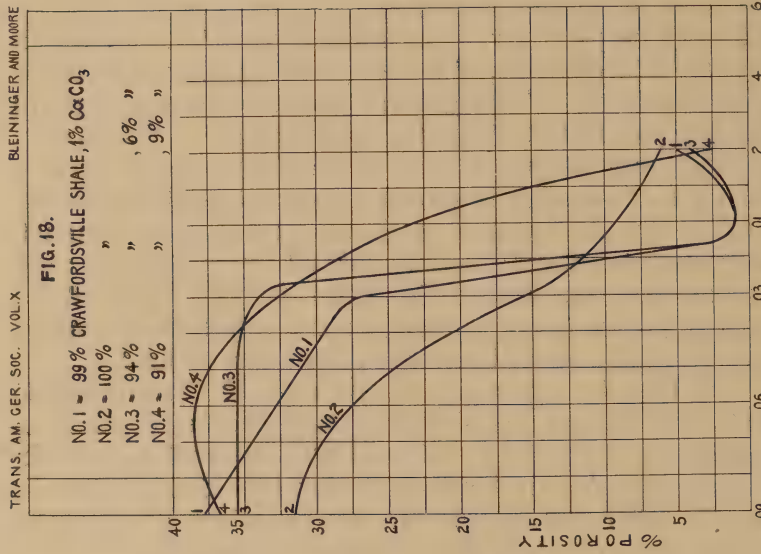
Shales. In the porosity curves of mixtures of Canton shale, Fig. 16, and whiting we observe that the lime begins to act as a refractory substance in percentages that vary with the temperature. In the Cone 06 curve almost the first addition of lime seems to increase the porosity, while

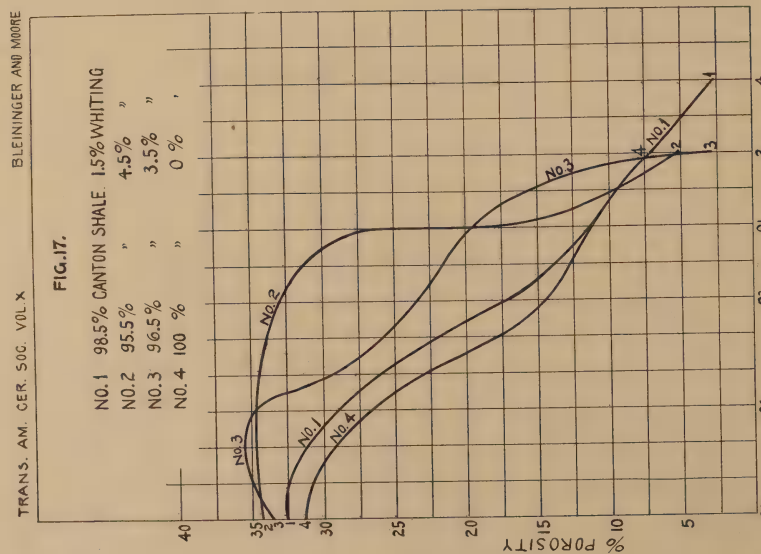
the increase in the Cone 01 and 2 curves begins with 1.5 and 4.5% respectively. The significance of the minimum with the 9% addition, if it really is a minimum, remains to be explained. From general considerations it appears that the porosity at about that point ought to decrease.

The rate at which this shale decreases in specific gravity and porosity is shown in Fig. 17, and brings out the fact that the porosity tends to increase up to Cone 06, and from this point on shows a rate of decrease slower than that of the pure shale. But after passing Cone 03 its vitrification becomes decidedly more rapid than that of unmixed shale, as we know to be the effect of lime.

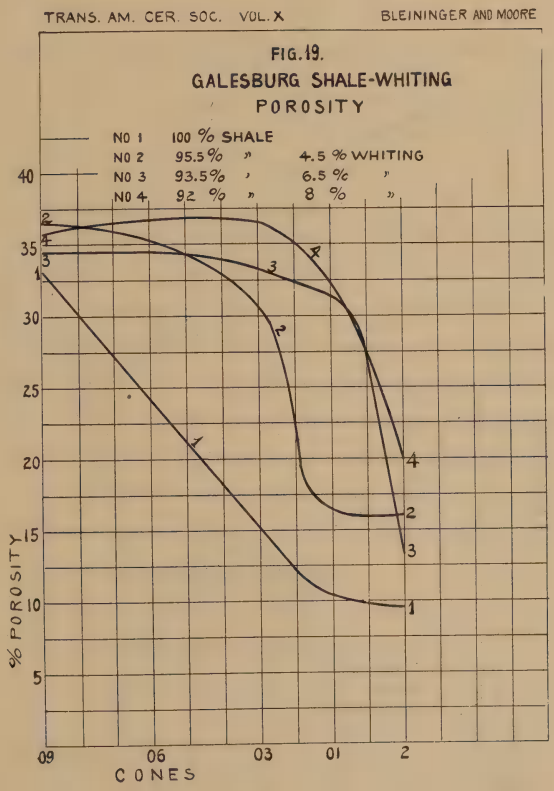
In Fig. 18, representing mixtures of Crawfordsville shale and whiting, we observe a very decided increase in porosity between Cones 06 and 03, followed by an extremely sudden drop between 03 and 01. The increase in porosity after vitrification has been reached is also quite marked in some of the lower lime mixtures.




TRANS. AM. CER. SOC. VOL. X
BLEININGER AND MOORE
FIG. 18.
NO. 1 ~ 99% CRAWFORDSVILLE SHALE, 1% $CaCO_3$
NO. 2 ~ 100 % " " , 6% "
NO. 3 ~ 94% " " , 9% "
NO. 4 ~ 91% " "
NO.1
NO.2
NO.3
NO.4
% POROSITY
CONES

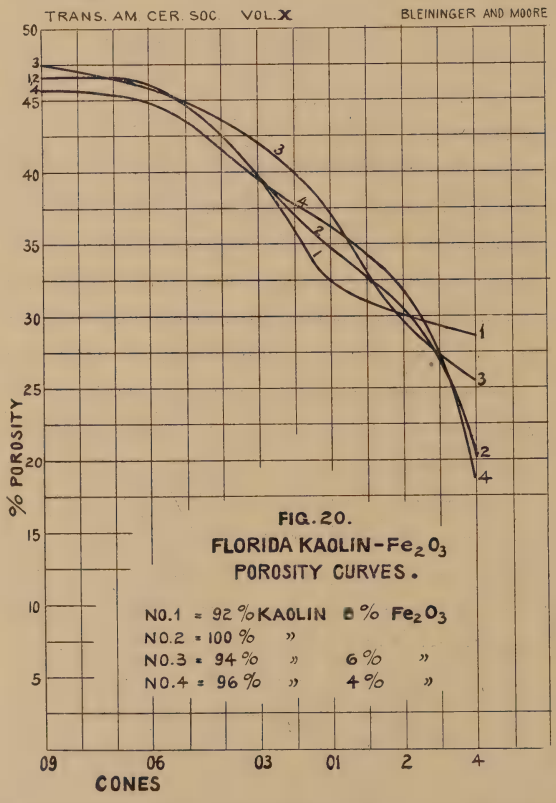

TRANS. AM. CER. SOC. VOL. X
BLEININGER AND MOORE
FIG. 17.
NO. 1 98.5% CANTON SHALE 1.5% WHITING
NO. 2 95.5% " 4.5% "
NO. 3 96.5% " 3.5% "
NO. 4 100 % " 0 % "
NO.1
NO.2
NO.3
NO.4
% POROSITY
CONES

The Galesburg shale, Fig. 19, was less affected by the lime added than the two other shales at Cone 2, but at Cone 4 the mixtures had gone considerably beyond viscous vitrification and had stuck to the saggers.



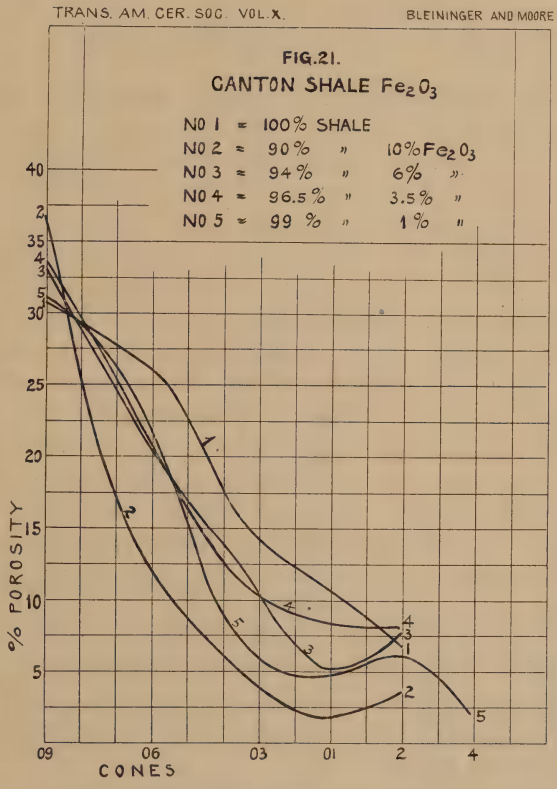
With regard to the effect of lime introduced as the carbonate we may say, therefore, that it is not a neutral, gradual flux, but evidently there are produced several combinations of lime with the other constituents of the clay which are available, which give risee to curves showing maximum and minimum points. This is the case especially with larger amounts of lime. This effect naturally is more

prominent at higher temperatures. The fluxing effect of small amounts of lime on high alumina clays is not marked at lower temperatures, as evidently such temperature as Cone 2 are not yet within the temperature zone of its activity.



In ferruginous shales containing lime the maximum fluxing effect is shown by not more than 5% of the carbonate. Any increase above this amount seems to produce refractoriness at temperatures up to Cone 2 inclusive. The amount of lime drawn into reaction increases with the temperature; while at Cone 06 it does not seem to have

taken part in the condensation of the body, at Cone 01 its effect is noticeable. In regard to its general behavior in a paving brick shale we must say, of course, that it is an undesirable constituent, not only because of its sudden fluxing effect, but also because of its tendency to produce vesicular structure.



ADDITION OF FERRIC OXIDE.

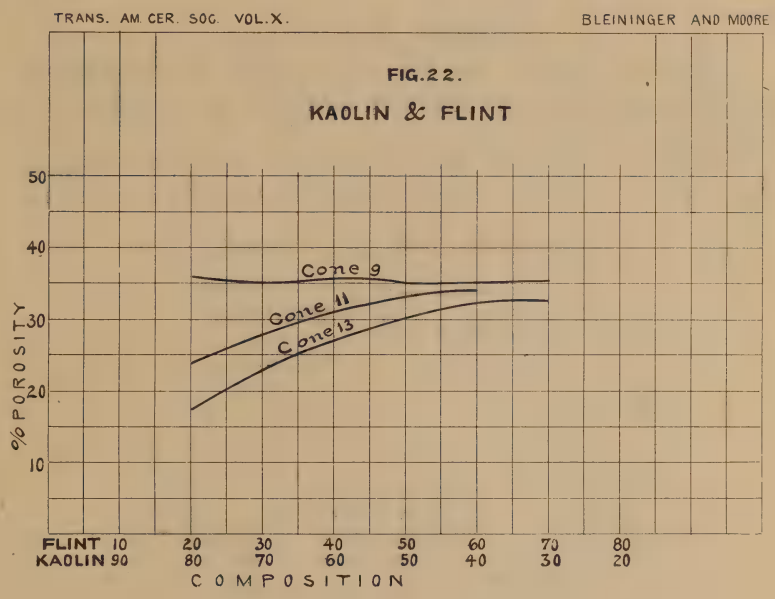
In the series in which we have mixtures of clay with increasing amounts of ferric oxide, it is evident that each increase in iron results in an increase of specific gravity, and hence specific gravity curves are of little value in this connection.

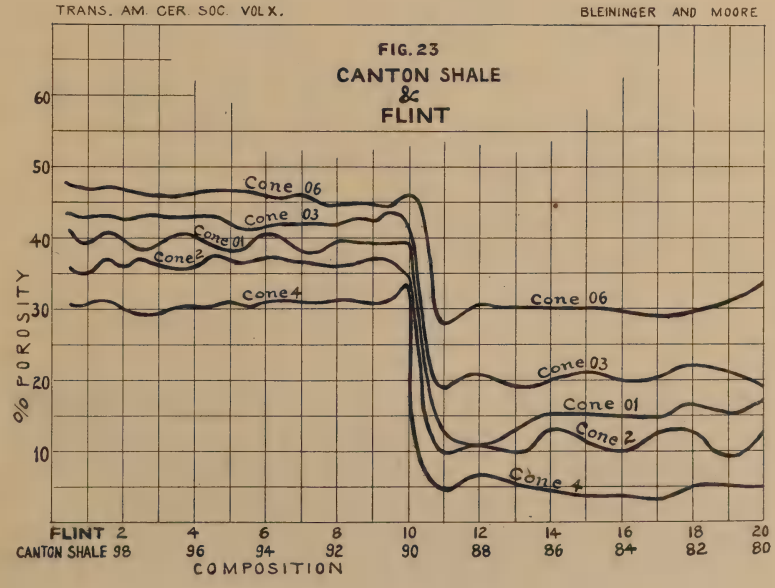
Florida Kaolin. From Fig. 20 we observe at once that iron oxide is by no means an active flux when combined with clay substance, for while a small amount seems to exert some fluxing action, its general tendency seems to be a rather indifferent behavior. The areas inclosd by the 100% kaolin and the kaolin-iron mixture curves give some measure of the fluxing effect of the ferric oxide. It is noted that in part of the curves the ferric oxide behaves as a refractory agent.

In the shale-ferric oxide series practically the same effects are observed. In the Cone 2 curve up to an addition of 2.5% of ferric oxide a small decrease in porosity is observed, after which the iron seems to behave as a neutral agent. More iron tends to make the clay more refractory up to a certain point. There is no doubt but that, if the iron were increased still more, one or minimum and maximum points would be reached, for in the 90% Canton shale—10% Fe_2O_3 curve the fluxing effect becomes quite marked. Fig. 21 shows the effect of the ferric oxide upon this shale by the areas enclosed between the two porosity curves. The other shales behave in much the same manner.

We may conclude from these results that ferric oxide is not an effective flux when combined with clay substance, nor has it a very marked influence upon ferruginous shales. In the first case, perhaps due to the lack of free silica, in the second due to the large amount of iron already present. At the same time the ferric oxide behaves as a slow acting and safe flux. An excess seems to promote the formation of a vesicular structure, and it might be that in the shale-iron oxide curves with varying percentages the increase in porosity is due to this cause.

The hypothetical case of adding iron oxide to clays in order to make them more suitable for the manufacture of paving brick seems, therefore, not to be well taken, though some patent specifications prescribe such a mixture.

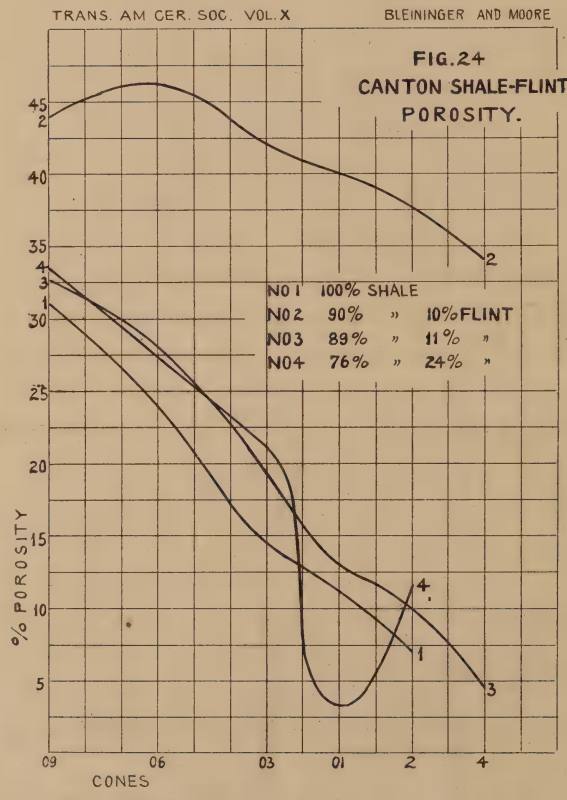

TRANS. AM. CER. SOC. VOL. X.
BLEININGER AND MOORE
FIG. 22.
KAOLIN & FLINT
% POROSITY
50
40
30
20
10
Cone 9
Cone 11
Cone 13
FLINT 10 20 30 40 50 60 70 80
KAOLIN 90 80 70 60 50 40 30 20
COMPOSITION


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG. 23
CANTON SHALE
&
FLINT
% POROSITY
60
50
40
30
20
10
Cone 06
Cone 03
Cone 01
Cone 2
Cone 4
Cone 06
Cone 03
Cone 01
Cone 2
Cone 4
FLINT 2 4 6 8 10 12 14 16 18 20
CANTON SHALE 98 96 94 92 90 88 86 84 82 80
COMPOSITION

ADDITION OF FLINT.

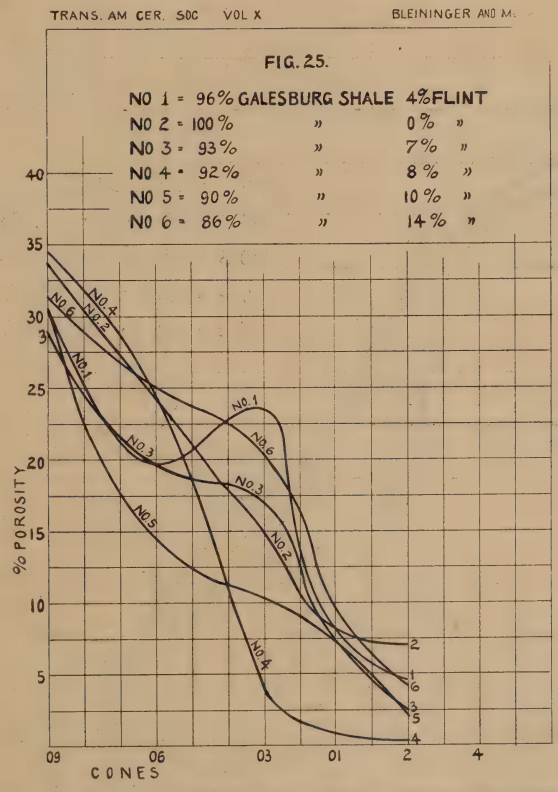
Florida Kaolin. As is to be expected, the kaolin-flint series produce curves showing increase in porosity with increase in flint, Fig. 22.

Shales. Mixtures of Canton shale and flint, Fig. 23, showed a remarkable drop in their porosity curve at the



composition, 90% shale, 11% flint. Up to this proportion the porosity of the shale mixtures for each temperature kept about constant. This drop is simultaneous in all of the temperature curves, and clearly indicates that a far reaching change took place at this point. The practical conclusion, hence, would be that 10% of fine flint acts as

a flux in this shale, forming probably an easily fusible silicate with the iron oxide and other fluxes. In mixtures of Galesburg shale and flint two drops were observed in the porosity curve, though neither one of them was well defined, one at 8%, the other at 18% flint. In the Craw-



fordsville shale mixtures the Cone 2 curve likewise showed two minimum points, one at 10%, the other at 19% flint. These points also were not as well defined as the point observed in the Canton shale, though more distinct than in the Galesburg shale.

Referring to the absolute fluxing effect, there is no gain as regards increase in fusibility by the addition of

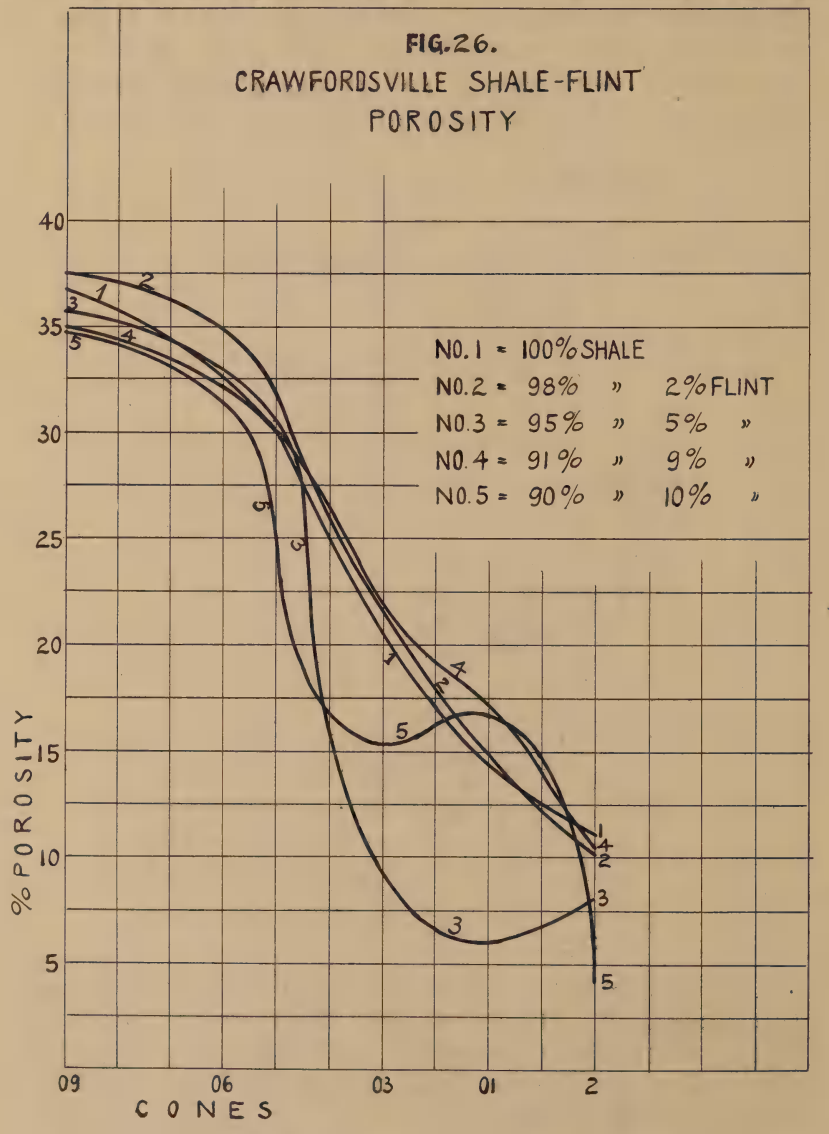
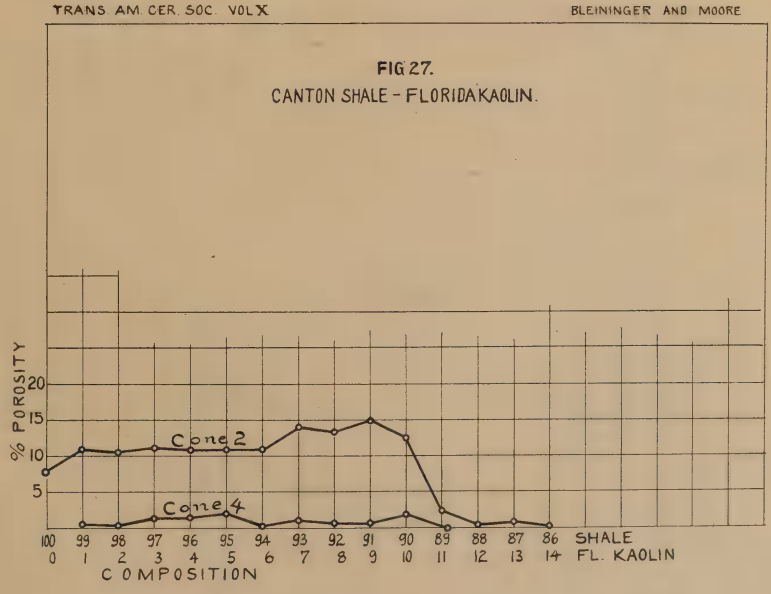


FIG.26.
CRAWFORDSVILLE SHALE-FLINT
POROSITY
NO.1 = 100% SHALE
NO.2 = 98% " 2% FLINT
NO.3 = 95% " 5% "
NO.4 = 91% " 9% "
NO.5 = 90% " 10% "
% POROSITY
40
35
30
25
20
15
10
5
09
06
03
01
2
CONES

flint to Canton shale. Any addition of flint at once makes the clay more refractory until 11% have been added, when the drop occurs. At the last point the mixture seems to be but a trifle more refractory than the unmixed shale, Fig. 24. The rate of vitrification does not seem to be affected; if at all, it is in the direction of safer burning.

The Galesburg shale mixtures with flint show a decidedly lower vitrification range than the pure shales, and it seems, hence, that in this case flint acts as a pronounced flux, Fig. 25.

In the Crawfordsville shale the flint acts distinctly as a flux up to 5%, and at the same time it disturbs the rate of vitrification unfavorably, Fig. 26. Above 5% the refractory character of flint appears, which is maintained until 10% have been added. In this case also the rate of vitrification is changed in an undesirable manner.


TRANS. AM. CER. SOC. VOL X
BLEININGER AND MOORE
FIG 27.
CANTON SHALE - FLORIDA KAOLIN.
% POROSITY
20
15
10
5
Cone 2
Cone 4
100 99 98 97 96 95 94 93 92 91 90 89 88 87 86 SHALE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 FL. KAOLIN
COMPOSITION

ADDITION OF ELORIDA KAOLIN.

Shales. The first addition of 1% of kaolin to Canton shale in the Cone 2 curve produced an increase in porosity which then kept practically constant until 6% had been added. At this point another slight rise in porosity took place. Between 10 and 11% a sudden drop in porosity was observed, and it is evident that the kaolin in this proportion exerts a decided fluxing action, Fig. 27.

In the Crawfordsville shale a rise in porosity at 2% and a drop at 3% is observed. With 15% of kaolin a very decided decrease in porosity is noted corresponding to the drop with 11% Canton shale, Fig. 28.

In the Galesburg shale we observe (Cone 2 curve) a drop in the porosity for the addition of 1% kaolin, followed by a rise, after which the curve has a slight upward slope. At the highest percentage of kaolin added, 15%, the minimum point, if there is one, has not been reached, though the curve suggests its presence, Fig. 29.

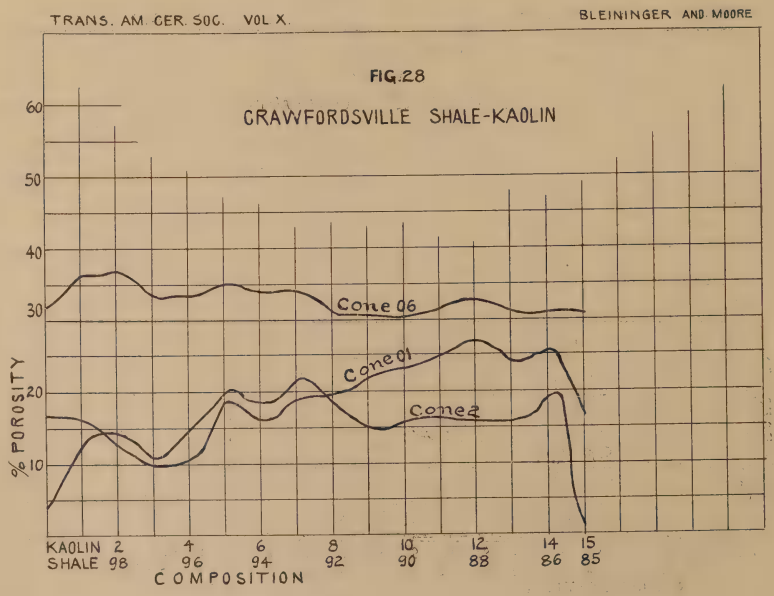
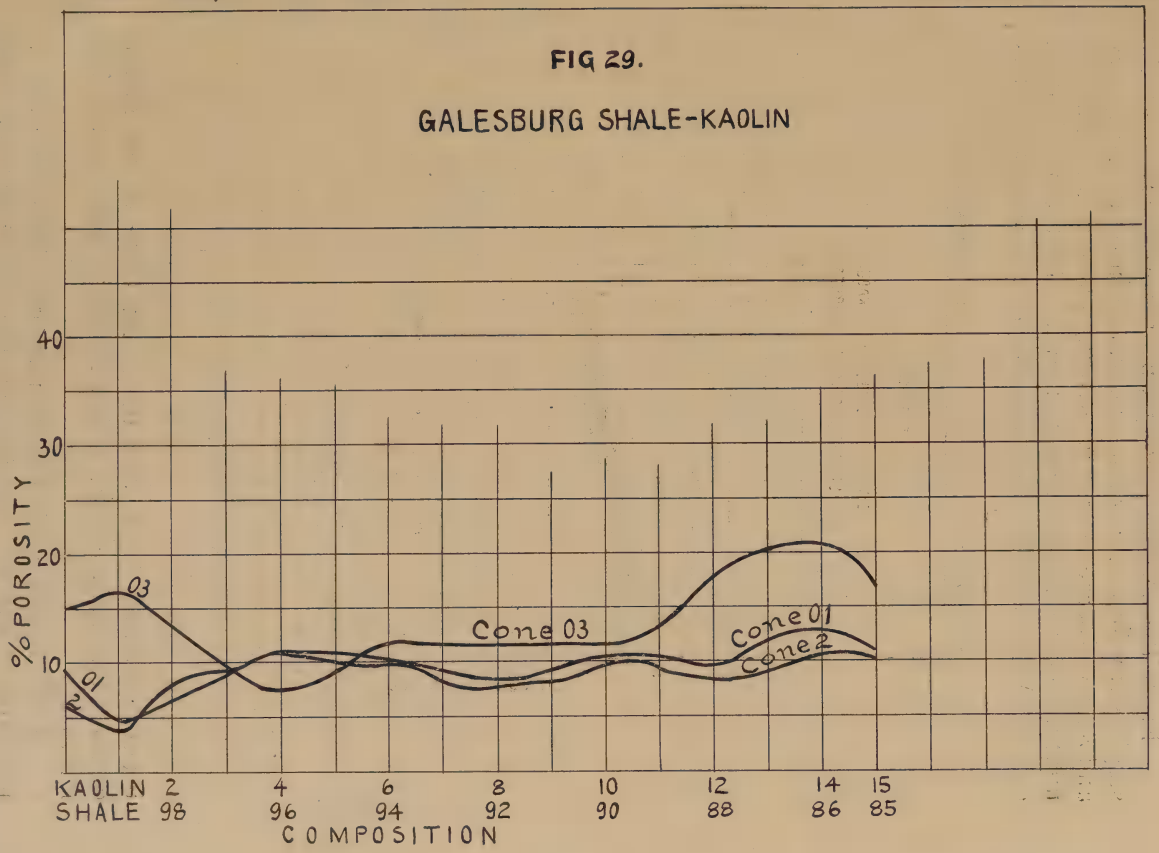
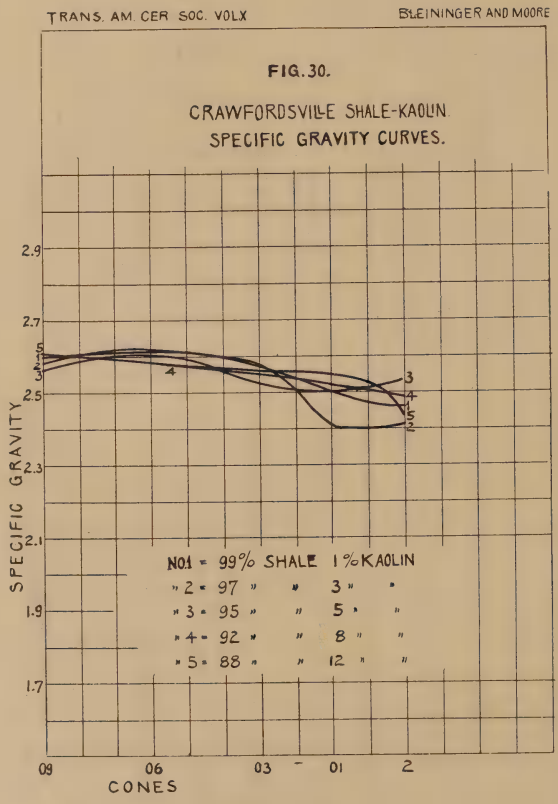


FIG 29.


GALESBURG SHALE-KAOLIN
% POROSITY
40
30
20
10
03
01
2
Cone 03
Cone 01
Cone 2
KAOLIN 2 4 6 8 10 12 14 15
SHALE 98 96 94 92 90 88 86 85
COMPOSITION

From the specific gravity and porosity curves of the single Crawfordsville shale and kaolin mixtures, Figs. 30 and 31, we observe several interesting phenomena. The 1% mixture curve is practically parallel to the pure shale curve. With the 3% mixture the kaolin acts as a flux

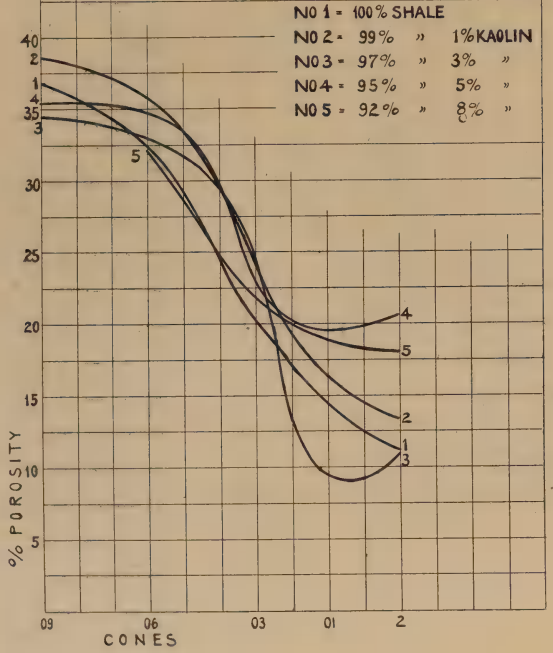


between Cones 09, 06, and 03-2. At Cone 01 we find a distinct minimum point, which is shown also in the 5% mixture.

The Canton shale-kaolin mixtures likewise show a minimum point at Cone 01, and the curves indicate that up to about 10% the clay substance does not exert any

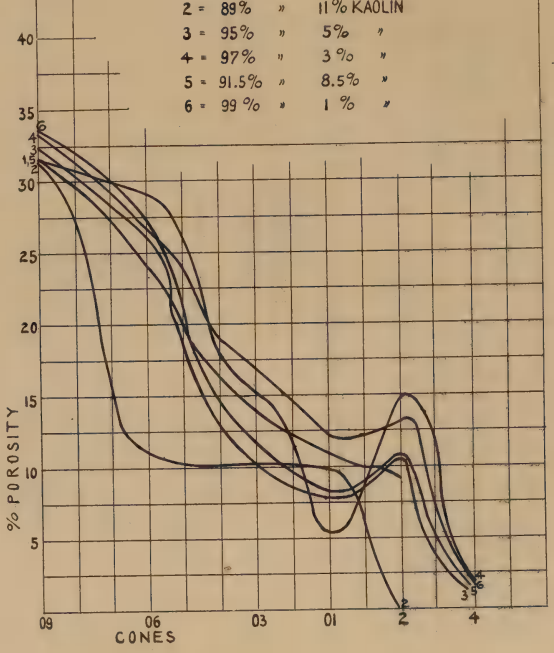
TRANS. AM. CER. SOC. VOL. X BLEININGER AND MOORE

FIG 31
CRAWFORDSVILLE SHALE-KAOLIN
POROSITY.

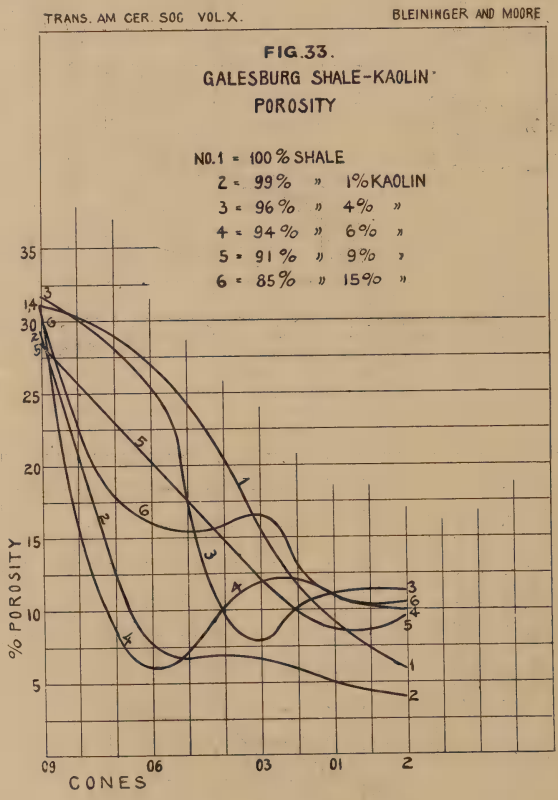


TRANS. AM CER. SOC. VOL. X. BLEININGER AND MOORE

FIG 32.
CANTON SHALE - Fla. KAOLIN.



influence upon the clay below Cone 03. The 11% mixture, however, shows a great drop in porosity, and here the kaolin behaves as a potent flux, Fig. 32. The fluxing power of kaolin in the Galesburg shale is shown by the 1% curve, and we note also in the curves up to 8% that this action

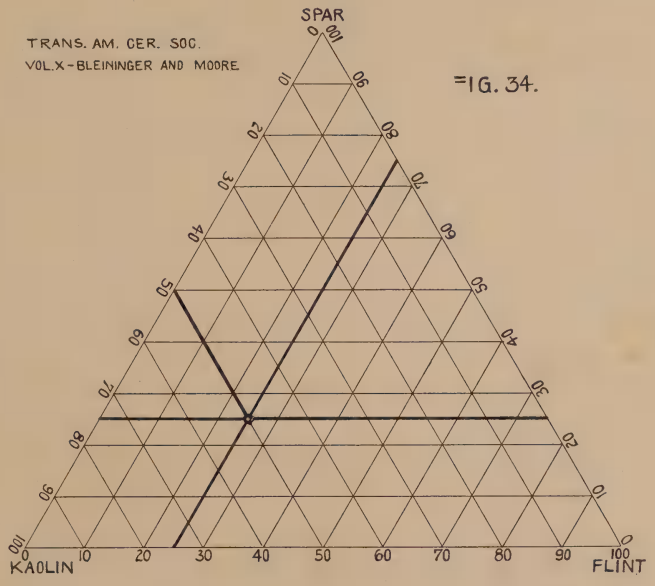


takes place at a low temperature, between Cones 09 and 03, the rate of decrease in porosity being quite steep.

It is shown clearly, hence, that different shales react quite differently towards kaolin, and it is not at all improbable that this might afford a means of differentiation between the structures of various shales.

ADDITION OF FELDSPAR-FLINT.

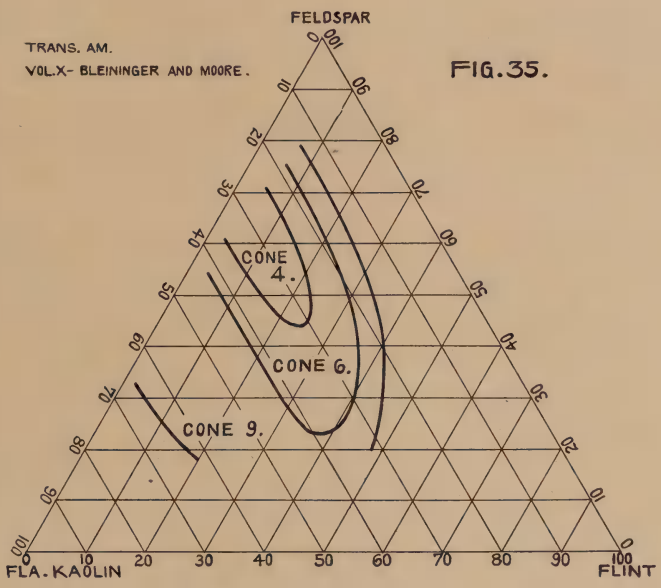
Kaolin. Mixtures of these three materials offer special interest to the clay worker inasmuch as they make up the bulk of our porcelain bodies. But the study of such a system becomes more complex, and hence the writers have resorted to the use of the triaxial diagram, which is a well known means of expressing three variable compositions



with the constant condition that the sum of the three components be equal to 100. The use of the triaxial diagram has been explained in our Transactions by Mr. H. E. Ashley (Vol. 7). To recapitulate briefly, let us call the lower left hand corner of the triangle, Fig. 34, the origin or 0 per cent of flint, then along the base of the triangle we measure the flint so that the right hand corner stands for 100% of flint. Continuing in the counter-clockwise direction we proceed to measure the feldspar along the right side of the triangle. This, of course, makes the 100%

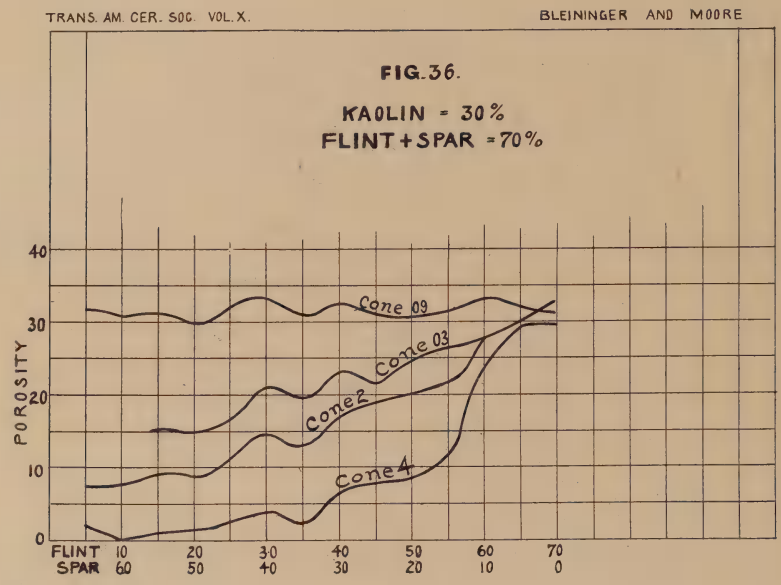
flint corner equal to 0% feldspar, and the apex of the triangle then becomes 100% feldspar and at the same time 0% kaolin. The latter thus is measured along the left side of the triangle and the lower left hand corner becomes equal to 100% kaolin. We might thus represent to ourselves the diagram made up of three triangles, of which the apices are respectively 100% flint, 100% feldspar, and 100% kaolin. The base of each triangle then would equal 0% of flint, feldspar and kaolin respectively. If hence we desire to plot flint we would measure along any line parallel to the base of the flint triangle, that is, parallel to the kaolin line. Similarly, we measure feldspar along any line parallel to the base of the feldspar triangle, that is, parallel to the flint line. The kaolin then would be measured along lines parallel to the feldspar line. Thus, a mixture consisting of 25% flint, 25% feldspar, and 50% kaolin would be measured as follows (Fig. 34). At the point 25% flint we follow a line drawn parallel to the kaolin line. We then proceed to the feldspar side and draw a line from the 25% point parallel to the flint side. The intersection of these two lines will be the point sought, for on drawing, from the intersection point, a line parallel to the feldspar side, it will strike the kaolin side at the 50% point. The point, hence, represents 25% flint, 25% feldspar, and 50% kaolin. Similarly any other mixture may be plotted.

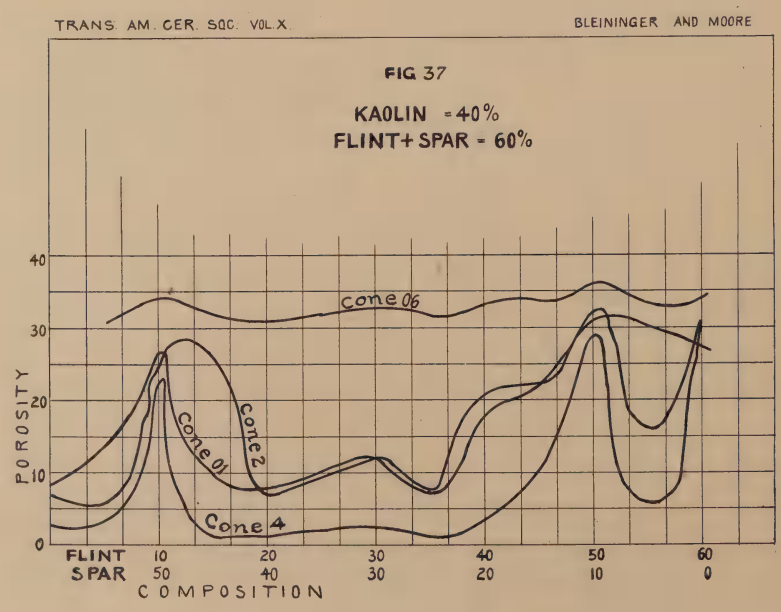
In the diagram we can now group together these mixtures, vitrifying at the same temperature by drawing lines connecting all mixtures whose vitrification point, that is, the point at which they absorb, not more than 1% of water is the same. For instance, by drawing a line around the area including all mixtures vitrifying at Cone 4 we have defined a thermal boundary, and the resulting curve we call the isothermal. By doing the same thing for the Cones 6 and 9 we obtain successive areas which increase in extent. This method, therefore, represents not only the compositions which may be expected to vitrify at a certain temperature from which the one most suitable for prac-

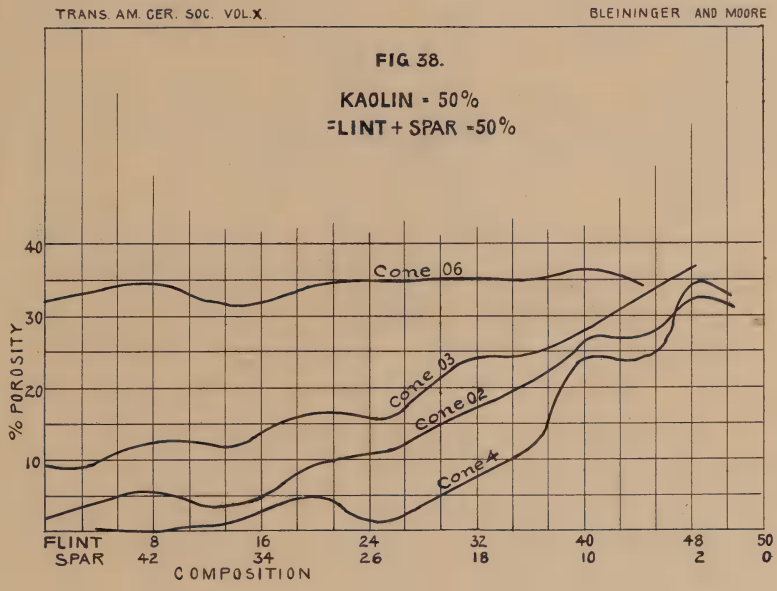


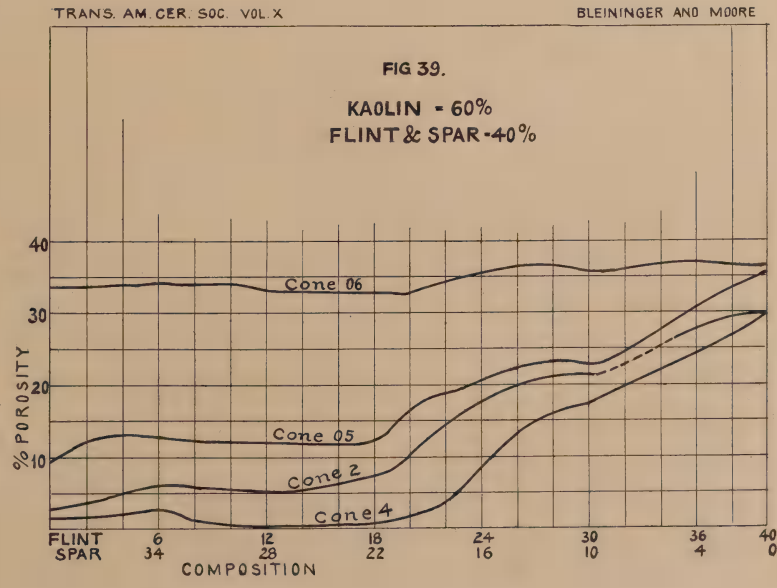
tical operation may be selected, but it also shows distinctly the intervals between the isothermals, thus expressing the range of the vitrification areas. Fig. 35 thus gives us a summary of the vitrification behavior of the system Florida kaolin-flint-feldspar, which needs no further explanation.

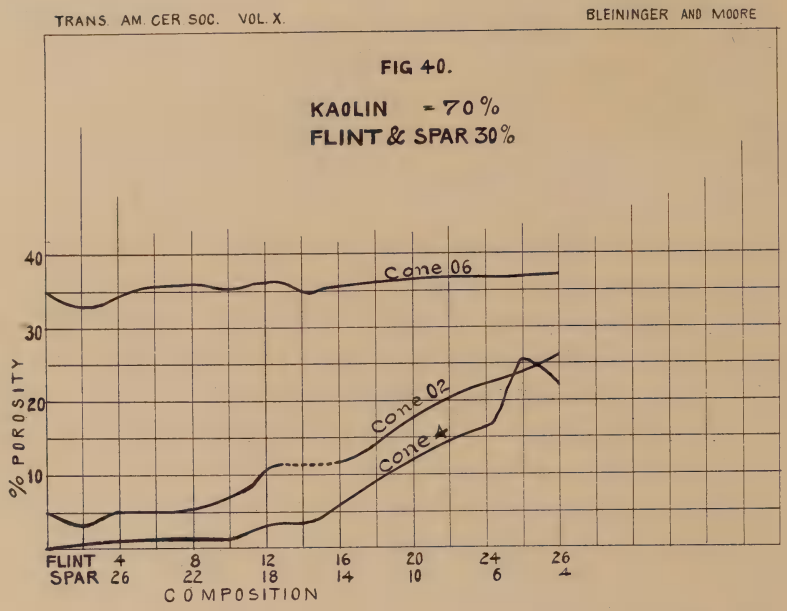
In Figs. 36, 37, 38, 39, 40, 41 we have mixtures of 30%, 40%, 50%, 60%, 70%, and 80% of Florida kaolin. In all the series excepting one, the 40% series, the porosity curves are fairly smooth. In this series two distinct maximum points are observed; one with 10% flint and 50% spar, the other with 50% flint and 10% spar. The cause of these two changes the writers do not venture to explain. In regard to the individual porosity curves of the kaolin-feldspar-flint series the rate of decrease in porosity becomes very sudden under two conditions, viz., in the kaolin-feldspar mixtures in the absence of flint, and in the mixtures containing but a small amount of flint compared with the amount of feldspar. This is more pronounced in the low kaolin series.

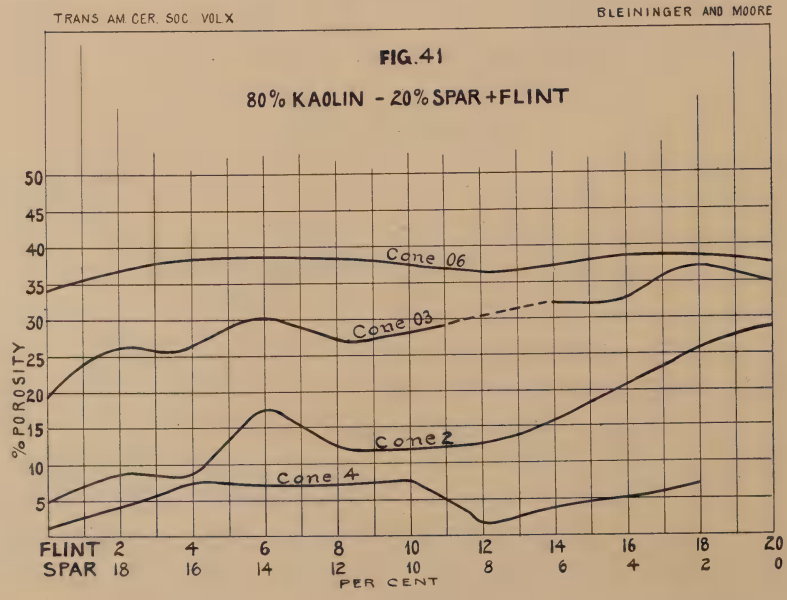

TRANS. AM. CER. SOC. VOL. X.
BLEININGER AND MOORE
FIG. 36.
KAOLIN = 30%
FLINT + SPAR = 70%
POROSITY
40
30
20
10
0
Cone 09
Cone 03
Cone 2
Cone 4
FLINT 10 20 30 40 50 60 70
SPAR 60 50 40 30 20 10 0


TRANS. AM. CER. SOC. VOL. X.
BLEININGER AND MOORE
FIG. 37
KAOLIN = 40%
FLINT + SPAR = 60%
POROSITY
40
30
20
10
0
Cone 06
Cone 01
Cone 2
Cone 4
FLINT 10 20 30 40 50 60
SPAR 50 40 30 20 10 0
COMPOSITION


TRANS. AM. CER. SOC. VOL. X.
BLEININGER AND MOORE
FIG 38.
KAOLIN - 50%
FLINT + SPAR - 50%
% POROSITY
40
30
20
10
Cone 06
Cone 03
Cone 02
Cone 4
FLINT 8 16 24 32 40 48 50
SPAR 42 34 26 18 10 2 0
COMPOSITION


TRANS. AM. CER. SOC. VOL. X
BLEININGER AND MOORE
FIG 39.
KAOLIN - 60%
FLINT & SPAR - 40%
% POROSITY
40
30
20
10
Cone 06
Cone 05
Cone 2
Cone 4
FLINT 6 12 18 24 30 36 40
SPAR 34 28 22 16 10 4 0
COMPOSITION


TRANS. AM. CER SOC. VOL. X.
BLEININGER AND MOORE
FIG 40.
KAOLIN = 70%
FLINT & SPAR 30%
% POROSITY
40
30
20
10
Cone 06
Cone 02
Cone 1
FLINT 4 8 12 16 20 24 26
SPAR 26 22 18 14 10 6 4
COMPOSITION


TRANS AM CER. SOC VOL X
BLEININGER AND MOORE
FIG. 41
80% KAOLIN - 20% SPAR + FLINT
% POROSITY
50
45
40
35
30
25
20
15
10
5
Cone 06
Cone 03
Cone 2
Cone 4
FLINT 2 4 6 8 10 12 14 16 18 20
SPAR 18 16 14 12 10 8 6 4 2 0
PER CENT

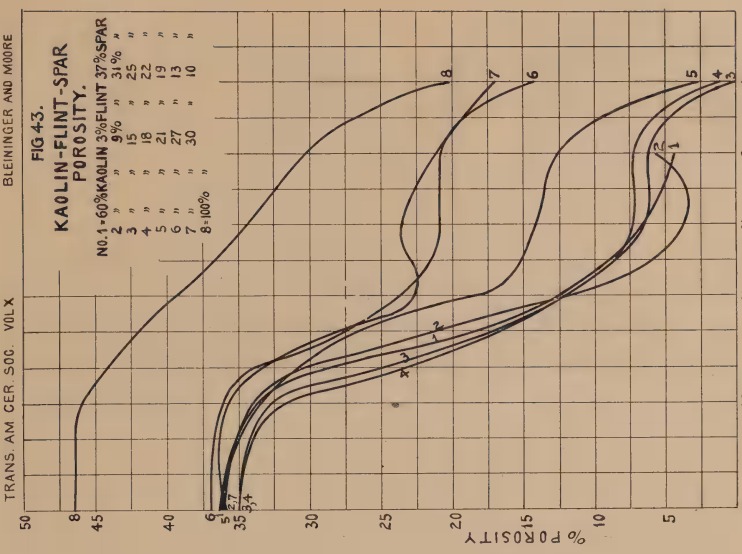


FIG 43.
KAOLIN-FLINT-SPAR
POROSITY.
NO. 1 = 60% KAOLIN 3% FLINT 37% SPAR
2 " " " 9% " 31% "
3 " " " 15 " 25 "
4 " " " 18 " 22 "
5 " " " 21 " 19 "
6 " " " 27 " 13 "
7 " " " 30 " 10 "
8 = 100% "
% POROSITY
CONES
TRANS. AM. CER. SOC. VOL X
BLEININGER AND MOORE

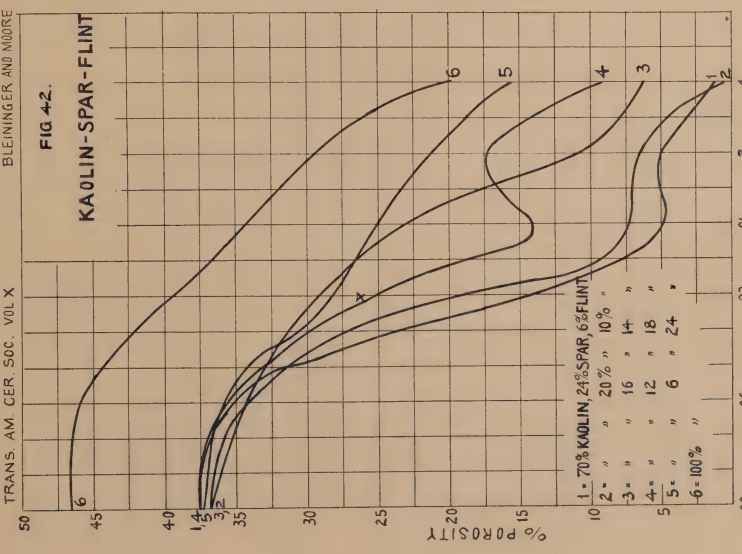
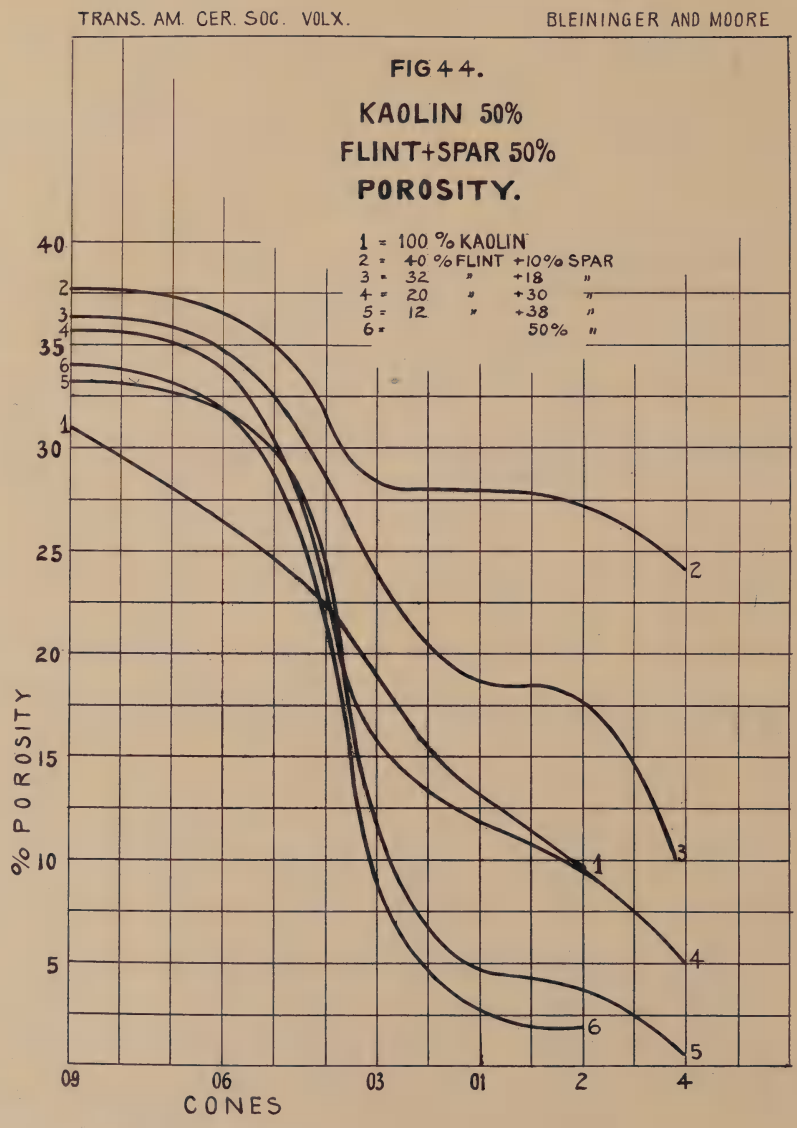


FIG 42.
KAOLIN-SPAR-FLINT
1 = 70% KAOLIN, 24% SPAR, 6% FLINT
2 " " 20 % " 10 % "
3 " " 16 " 14 " "
4 " " 12 " 18 " "
5 " " 6 " 24 " "
6 = 100% "
% POROSITY
CONES
TRANS. AM. CER. SOC. VOL X
BLEININGER AND MOORE


TRANS. AM. CER. SOC. VOLX.
BLEININGER AND MOORE
FIG 44.
KAOLIN 50%
FLINT+SPAR 50%
POROSITY.
1 = 100 % KAOLIN
2 = 40 % FLINT +10% SPAR
3 = 32 " +18 "
4 = 20 " +30 "
5 = 12 " +38 "
6 = 50% "
% POROSITY
40
35
30
25
20
15
10
5
09
06
03
01
2
4
CONES

As the flint increases the curves assume a gentle slope. An illustration of this behavior is shown by Figs. 42, 43, 44. It is also an interesting fact that feldspar behaves as a powerful flux at such low temperatures as Cones 06 and 03. The writers find it impossible to discuss the many curves available from these series without greatly exceeding the limits of this paper. One more fact might be mentioned, however, and this is the tendency of high feldspar mixtures to become vesicular, even before total vitrification is reached, thus obscuring the real changes taking place in the molecular body structure.

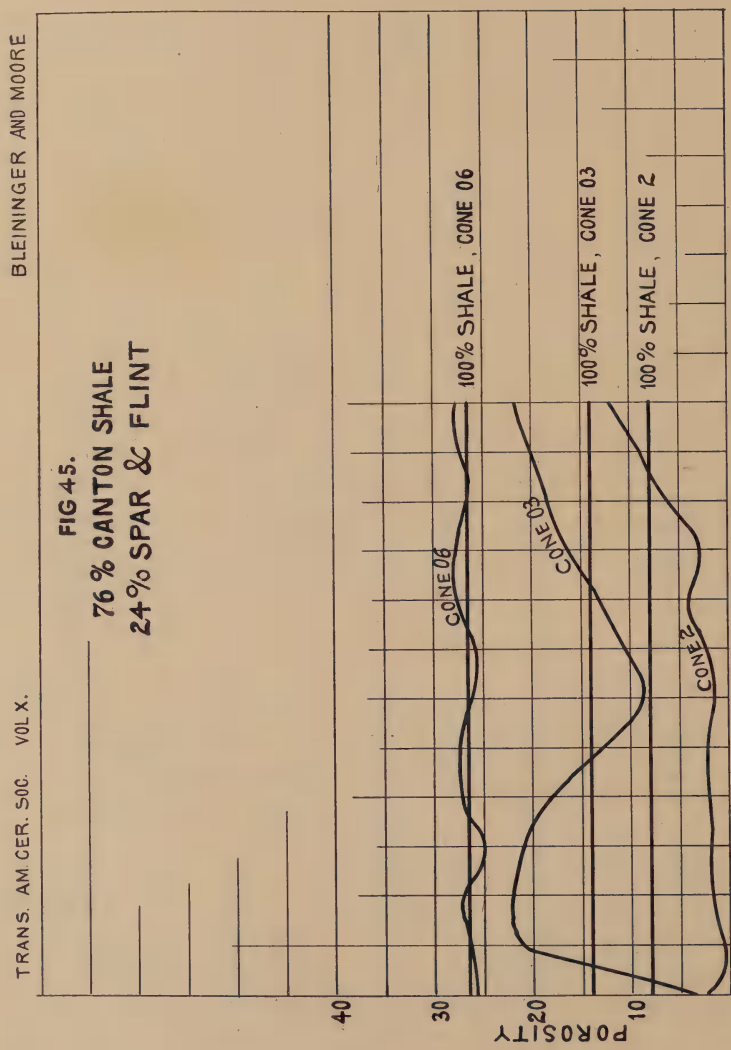
Shale. The effect of a feldspar-flint mixture may be observed in Fig. 45, where we have 76% Canton shale and 24% of feldspar and flint. It is seen that even a mixture of 7% of spar and 17% of flint exerts a fluxing action upon the shale.

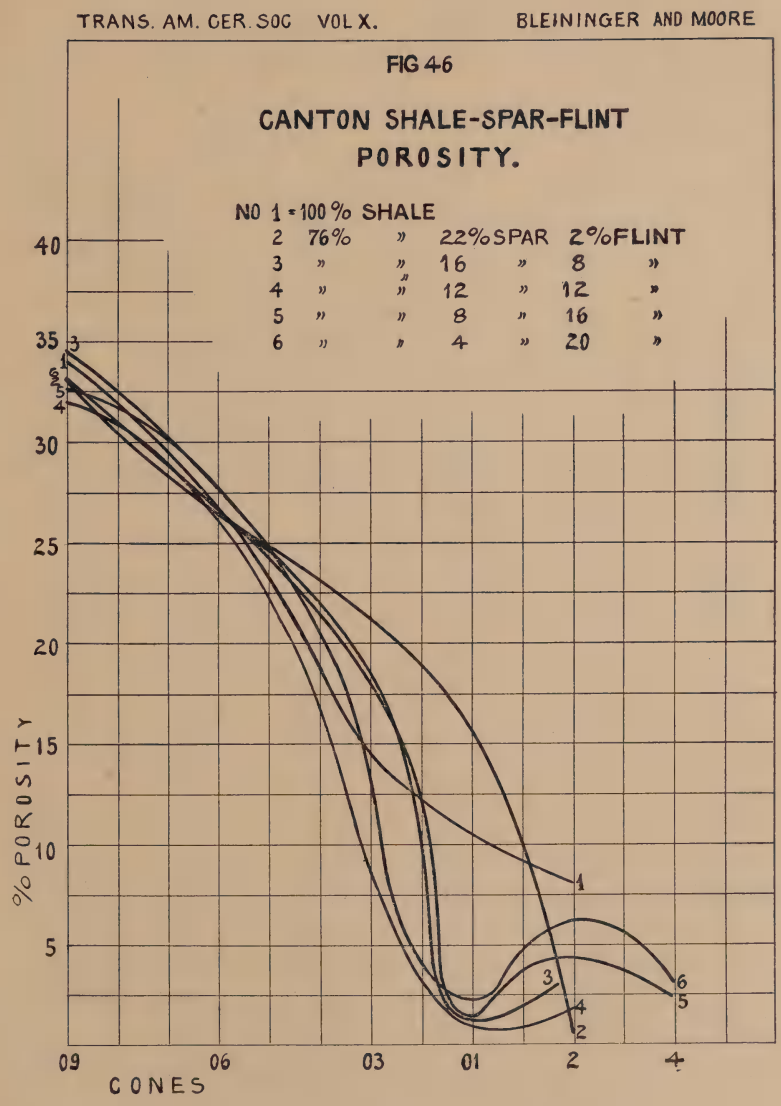
Similar effects are observed on the Galesburg and Crawfordsville shales. Fig. 46 shows the vitrification of some Canton shale-spar-flint mixtures in which the fluxing effect of these components at Cone 2 becomes quite evident.

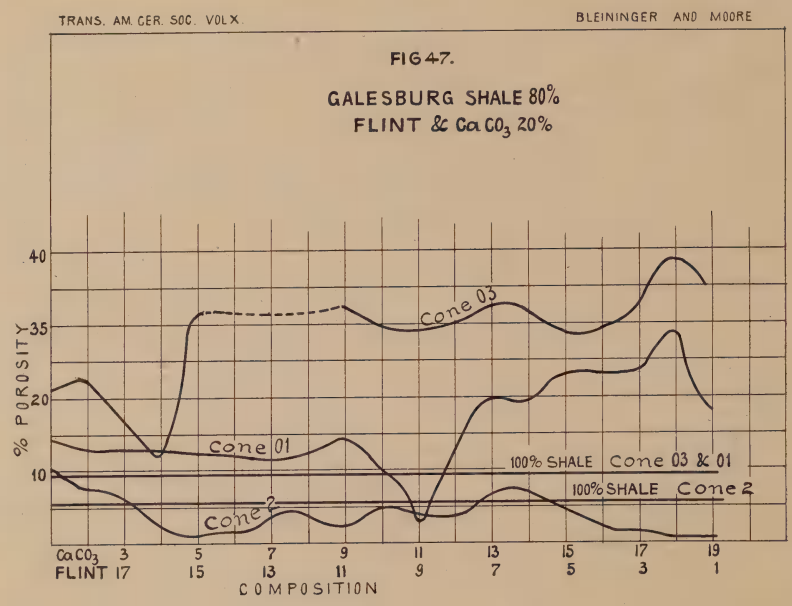
ADDITION OF LIME SILICA.

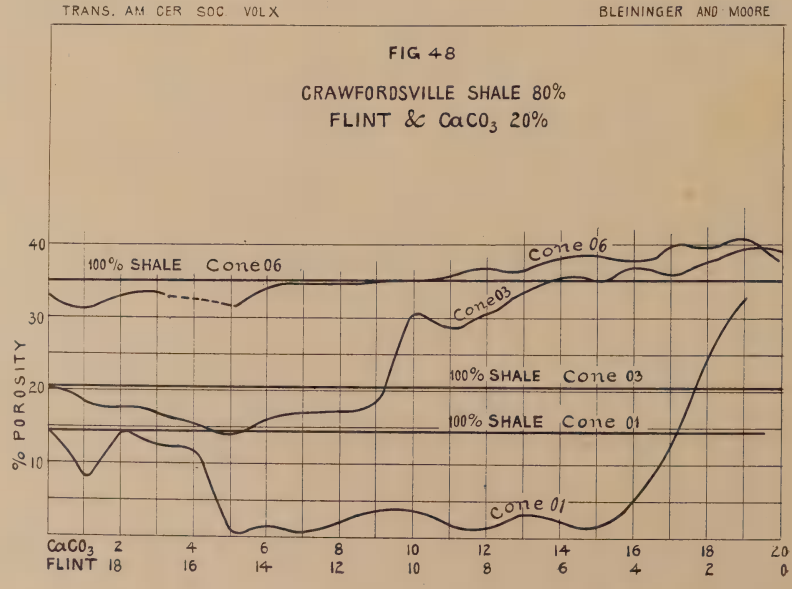
Shales. The effect of lime-silica upon the Galesburg and Crawfordsville shales is shown in Figs. 47 and 48. A mixture of 5% whiting and 15% flint has evidently lowered the vitrification point of the Galesburg shale to Cone 2 and that of the Crawfordsville shale to 01. In each case this is accomplished at the sacrifice of the safe to a rapid rate of vitrification. The presence of the silica seems to have a slight modifying effect since the curves are not so abrupt as they would be if the lime were added alone.

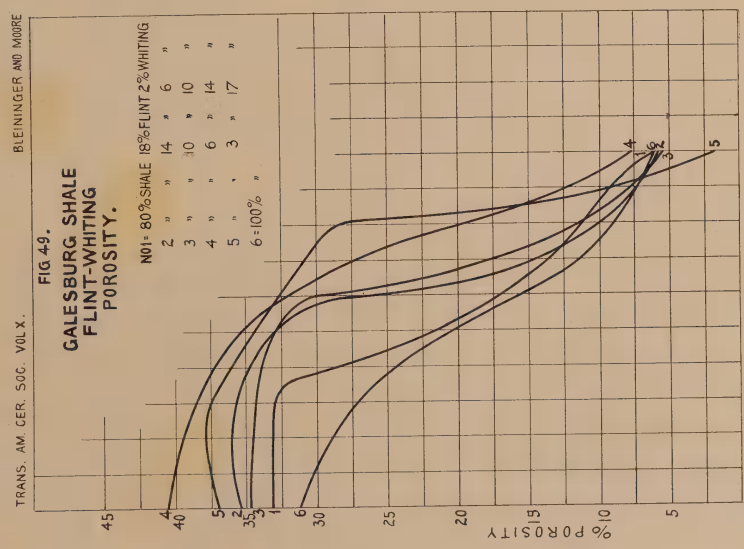
In Figs. 49, 50 and 50a we find assembled some of the vitrification curves of these shales blended with varying amounts of flint and whiting.

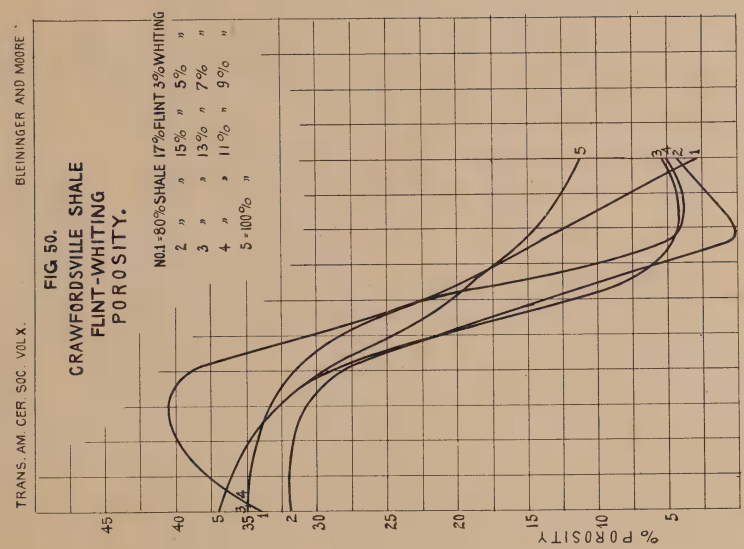

TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 45.
76 % CANTON SHALE
24 % SPAR & FLINT
100% SHALE, CONE 06
100% SHALE, CONE 03
100% SHALE, CONE 2
CONE 06
CONE 03
CONE 2
POROSITY
40
30
20
10
0 FELDSPAR
24 FLINT
24 20 16 12 8 4 0
0 4 8 12 16 20 24

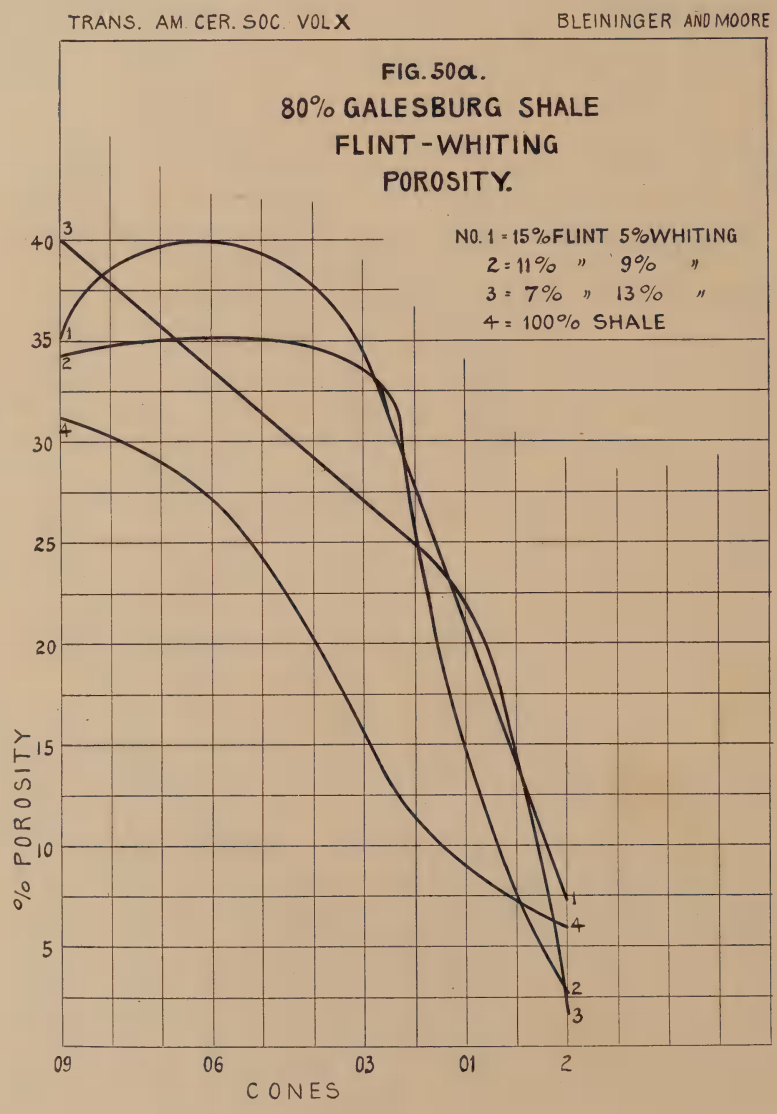

TRANS. AM. CER. SOC VOL X.
BLEININGER AND MOORE
FIG 46
CANTON SHALE-SPAR-FLINT
POROSITY.
NO 1 = 100 % SHALE
2 76% " 22% SPAR 2% FLINT
3 " " 16 " 8 "
4 " " 12 " 12 "
5 " " 8 " 16 "
6 " " 4 " 20 "
% POROSITY
40
35
30
25
20
15
10
5
09
06
03
01
2
4
CONES


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 47.
GALESBURG SHALE 80%
FLINT & $CaCO_3$ 20%
% POROSITY
40
35
20
10
Cone 03
Cone 01
Cone 2
100% SHALE Cone 03 & 01
100% SHALE Cone 2
$CaCO_3$ 3 5 7 9 11 13 15 17 19
FLINT 17 15 13 11 9 7 5 3 1
COMPOSITION


TRANS. AM CER SOC VOL X
BLEININGER AND MOORE
FIG 48
CRAWFORDSVILLE SHALE 80%
FLINT & $CaCO_3$ 20%
% POROSITY
40
30
20
10
100% SHALE Cone 06
Cone 06
Cone 03
100% SHALE Cone 03
100% SHALE Cone 01
Cone 01
$CaCO_3$ 2 4 6 8 10 12 14 16 18 20
FLINT 18 16 14 12 10 8 6 4 2 0


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 49.
GALESBURG SHALE
FLINT-WHITING
POROSITY.
No1= 80% SHALE 18% FLINT 2% WHITING
2 " " 14 " 6 "
3 " " 10 " 10 "
4 " " 6 " 14 "
5 " " 3 " 17 "
6 = 100% "
% POROSITY
CONES
09 06 03 01 2
45 40 35 30 25 20 15 10 5

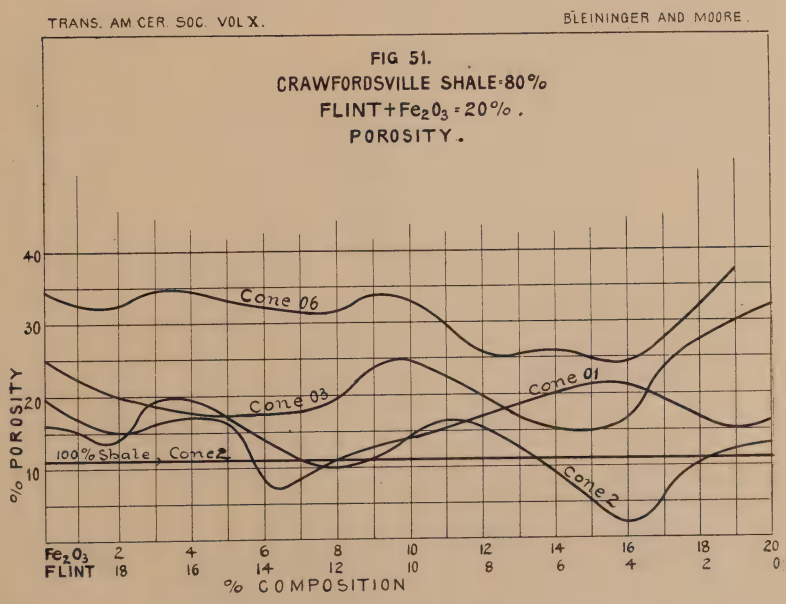

TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 50.
CRAWFORDSVILLE SHALE
FLINT-WHITING
POROSITY.
No1 = 80% SHALE 17% FLINT 3% WHITING
2 " " 15% " 5% "
3 " " 13% " 7% "
4 " " 11% " 9% "
5 = 100% "
% POROSITY
CONES
09 06 03 01 2
45 40 35 30 25 20 15 10 5


TRANS. AM. CER. SOC. VOL X
BLEININGER AND MOORE
FIG. 50a.
80% GALESBURG SHALE
FLINT-WHITING
POROSITY.
NO. 1 = 15% FLINT 5% WHITING
2 = 11% " 9% "
3 = 7% " 13% "
4 = 100% SHALE
% POROSITY
40
35
30
25
20
15
10
5
09
06
03
01
2
CONES

ADDITION OF FERRIC OXIDE-FLINT.

Shales. In Fig. 51, showing the porosity curves of 80% Crawfordsville shale and 20% ferric oxide and flint, we observe at once that the reactions appear complex, and by no means continuous. In the Cone 2 curve we have three distinct minimum points. We also observe that the reactions, whatever they may be, begin at a low temperature, since the curves lie very close together. With 6% Fe_2O_3 even the Cone 01 curve has come considerably below the porosity shown in the normal shale at Cone 2. We observe in this connection the fact that at Cone 01 the shale shows a lower porosity than at Cone 2. This increase in porosity at the higher temperature appears to be due to vesicular structure, which is observed even before vitrification is reached at any point. With 16% Fe_2O_3 the shale mixture reaches complete vitrification at Cone 2, at which temperature the normal shale has a porosity of 11%.

In a mixture of 75% Canton shale and 25% ferric



oxide and flint, Fig. 52, we observe somewhat similar conditions. Complete vitrification is reached here as low as Cone 01, at which temperature the normal shale has a porosity of 12%. This point occurs with a mixture of 10% Fe_2O_3, 15% flint, that is, with a ratio of 2:3.

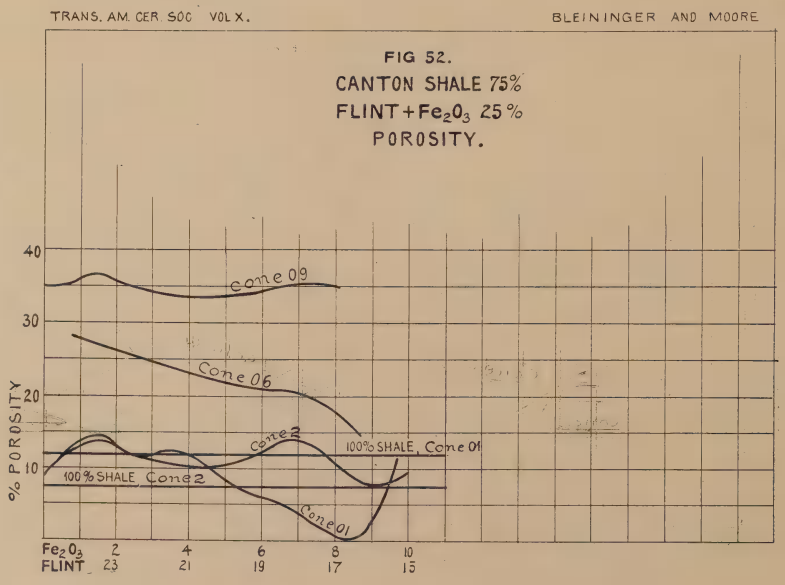
The Galesburg shale seems to behave more regularly than the preceding clays, and does not appear to produce the vesicular structure observed in the former. No decided change seems to take place at Cone 2 for the changes in the iron-flint ratio, Fig. 53.

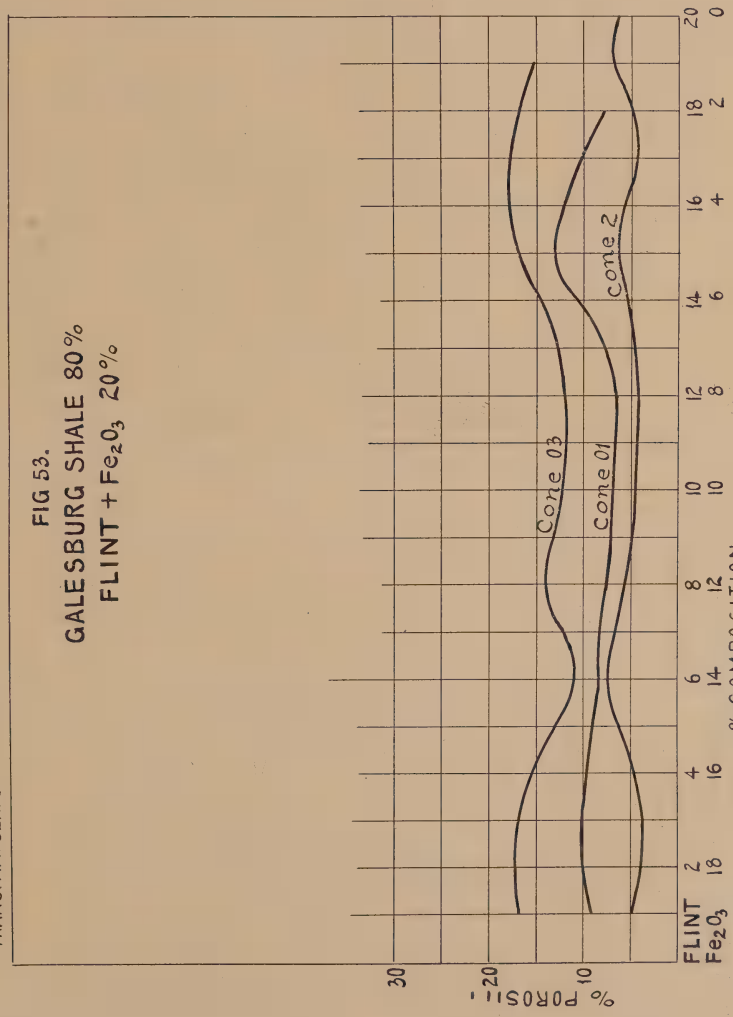
The individual vitrification curves of these shales-iron-flint combinations are illustrated in Figs. 54, 55, 56.

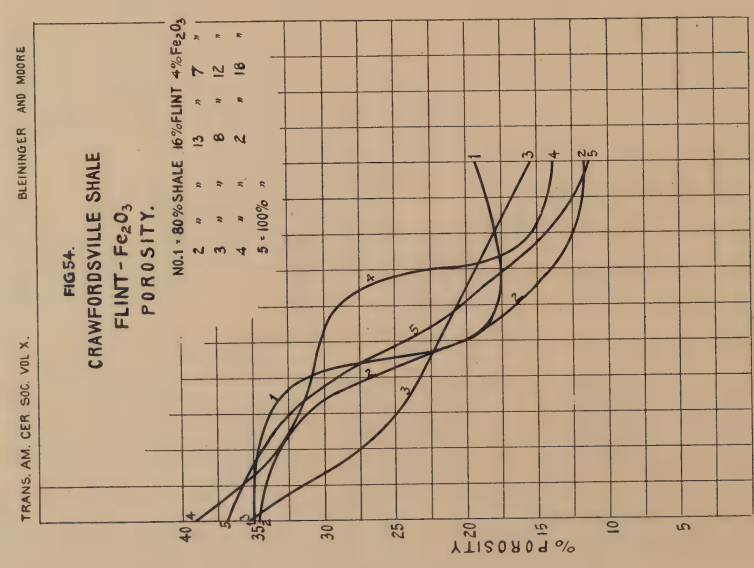
Similar results have been obtained by Worcester in experiments involving the production of mixtures of red Bedford shale and ground Berea grit.

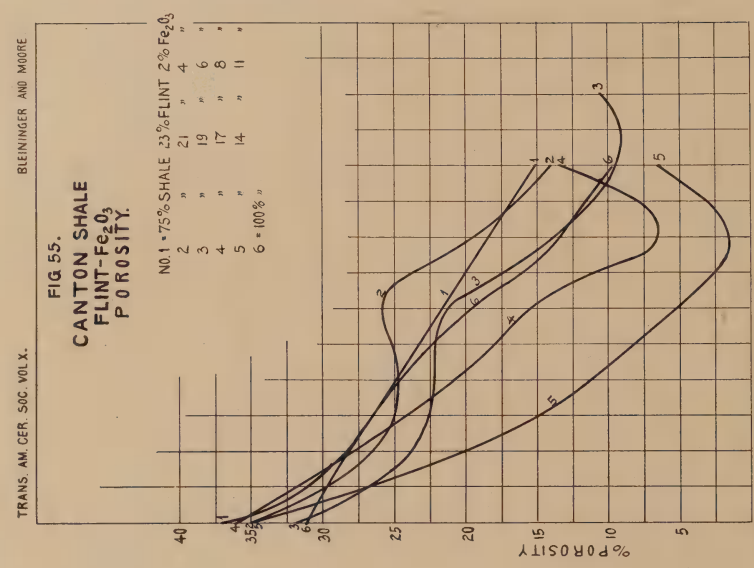
ADDITION OF FERRIC OXIDE-LIME.

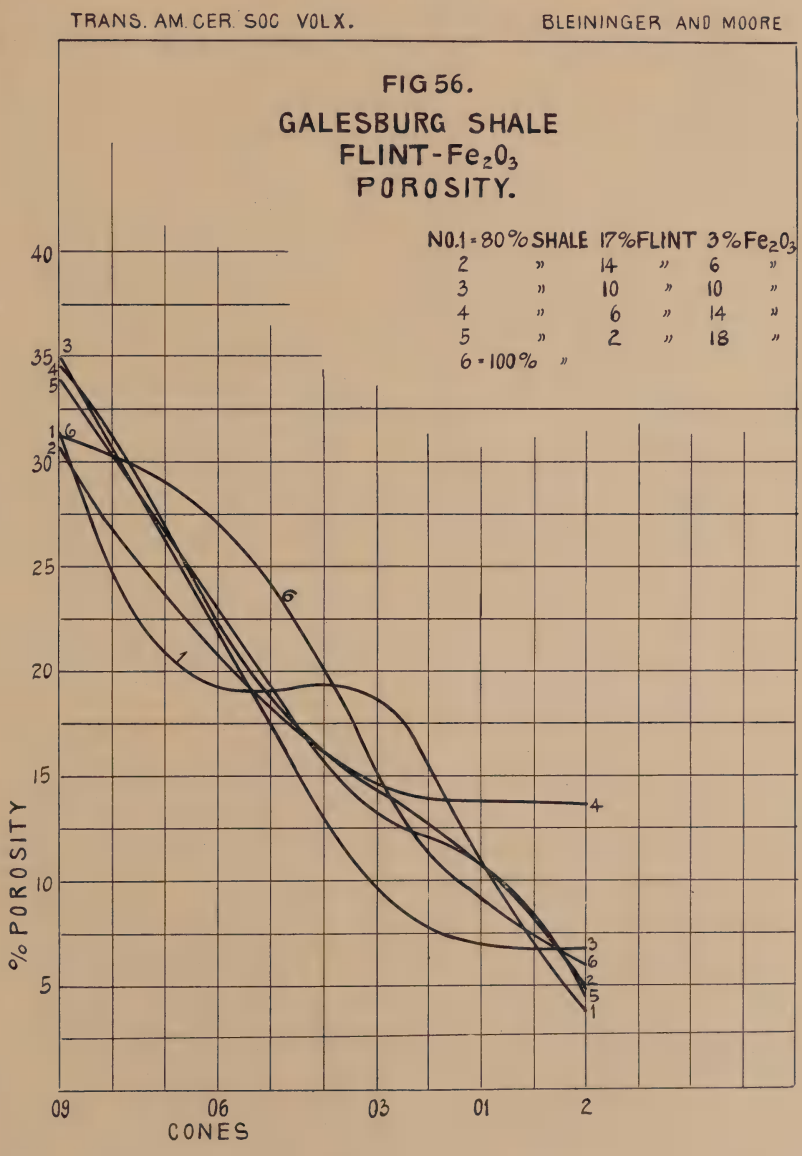
Shales. Here we observe that in a mixture of 90% of Crawfordsville shale, 3% Fe_2O_3 and 7% whiting have




TRANS. AM CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 53.
GALESBURG SHALE 80%
FLINT + Fe_2O_3 20%
% POROSITY
30
20
10
Cone 03
Cone 01
Cone 2
FLINT 2 4 6 8 10 12 14 16 18 20
Fe_2O_3 18 16 14 12 10 8 6 4 2 0
% COMPOSITION


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 54.
CRAWFORDSVILLE SHALE
FLINT - Fe_2O_3
POROSITY.
NO.1 - 80% SHALE 16% FLINT 4% Fe_2O_3
2 " " 13 " 7 "
3 " " 8 " 12 "
4 " " 2 " 18 "
5 - 100% "
% POROSITY
CONES
40
35
30
25
20
15
10
5
09
06
03
01
2
4


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 55.
CANTON SHALE
FLINT - Fe_2O_3
POROSITY.
NO.1 - 75% SHALE 23% FLINT 2% Fe_2O_3
2 " 21 " 4 "
3 " 19 " 6 "
4 " 17 " 8 "
5 " 14 " 11 "
6 = 100% "
% POROSITY
CONES
40
35
30
25
20
15
10
5
09
06
03
01
2
4


TRANS. AM. CER. SOC VOL X.
BLEININGER AND MOORE
FIG 56.
GALESBURG SHALE
FLINT-Fe_2O_3
POROSITY.
No.1 = 80% SHALE 17% FLINT 3% Fe_2O_3
2 " 14 " 6 "
3 " 10 " 10 "
4 " 6 " 14 "
5 " 2 " 18 "
6 = 100% "
% POROSITY
40
35
30
25
20
15
10
5
09
06
03
01
2
CONES

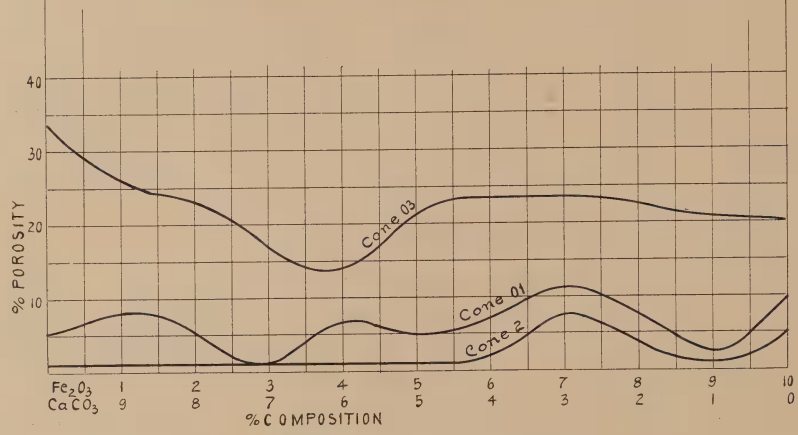
TRANS. AM. CER. SOC. VOL X

FIG 57.

CRAWFORDSVILLE SHALE=90%

$CaCO_3 + Fe_2O_3 = 10\%$

POROSITY.



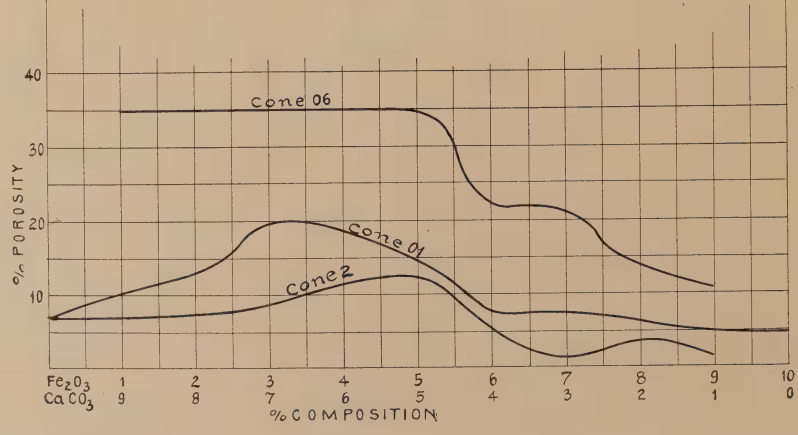
TRANS. AM. CER. SOC. VOL X.

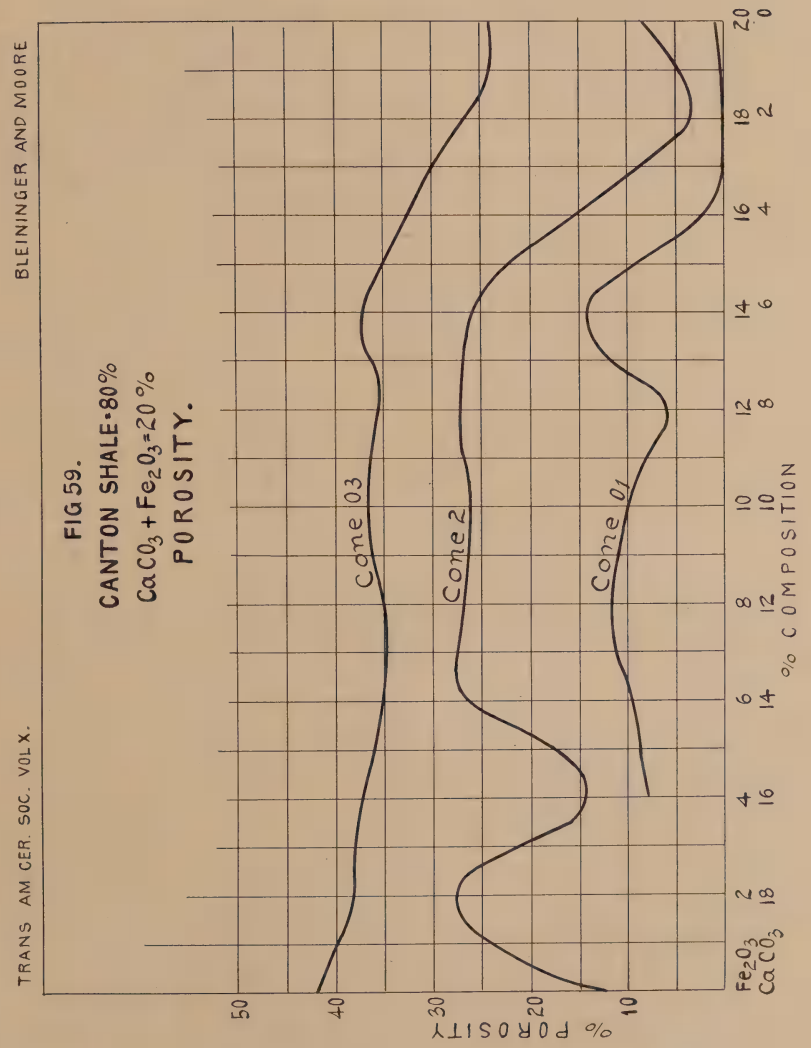
FIG 58.

GALESBURG SHALE=90%

$CaCO_3 + Fe_2O_3 = 10\%$

POROSITY.




TRANS AM CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 59.
CANTON SHALE·80%
$CaCO_3 + Fe_2O_3$=20%
POROSITY.
Cone 03
Cone 2
Cone 01
% POROSITY
50
40
30
20
10
Fe_2O_3 2 4 6 8 10 12 14 16 18 20
$CaCO_3$ 18 16 14 12 10 8 6 4 2 0
% COMPOSITION

brought the vitrification down to Cone 01. Increase in ferric oxide causes the vitrification point to rise until the mixture, 9% Fe_2O_3 and 1% whiting is reached, where we have a second minimum point. The Cone 01 and Cone 2 curves, it will be observed, are very close together, Fig. 57.

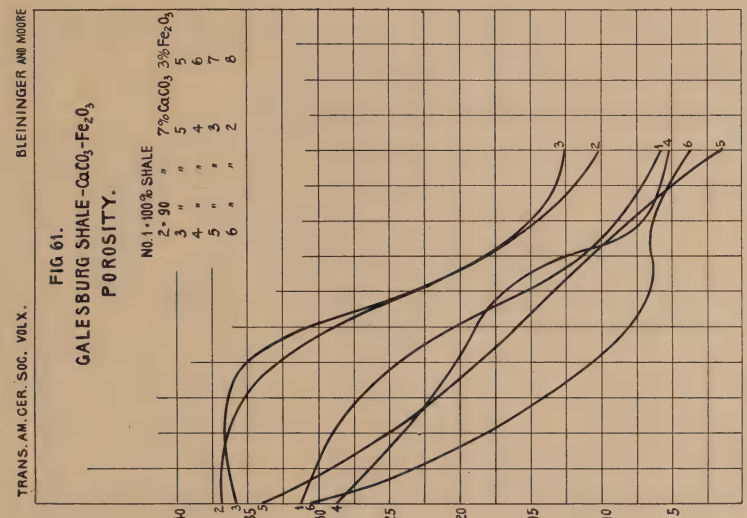
In the Galesburg shale conditions appear to be somewhat different and we have, within the range studied, only one minimum point which is close to 6% Fe_2O_3, 4% whiting in the Cone 01 curve. In the Cone 2 curve it has advanced to 7% Fe_2O_3 and 3% whiting, Fig. 58.

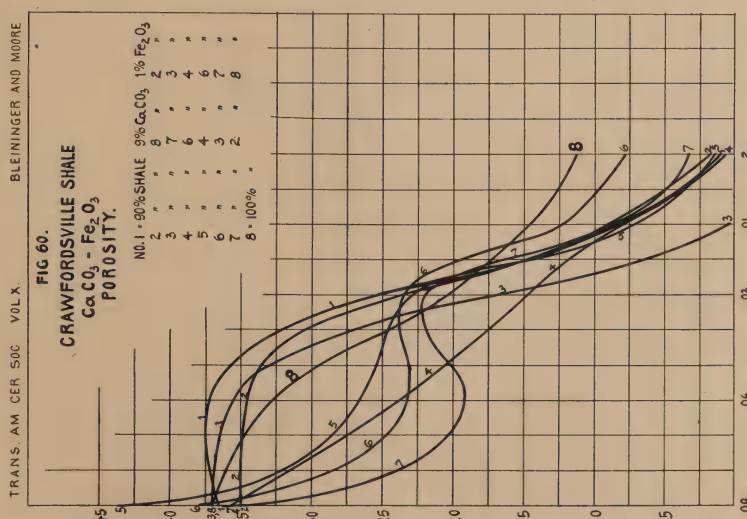
The Canton shale seems to be more sensitive to such additions, as is shown in Fig. 59, where it appears that the shale has been rendered vesicular in structure at Cone 2. It is especially peculiar that this should be the case, since Cone 01 does not seem to have produced vitrification. It is possible that the vitrification range is so narrow that it was missed in the experiments. Yet this seems hardly probable. The natural conclusion would be that the formation of "blebs" took place before general vitrification set in.

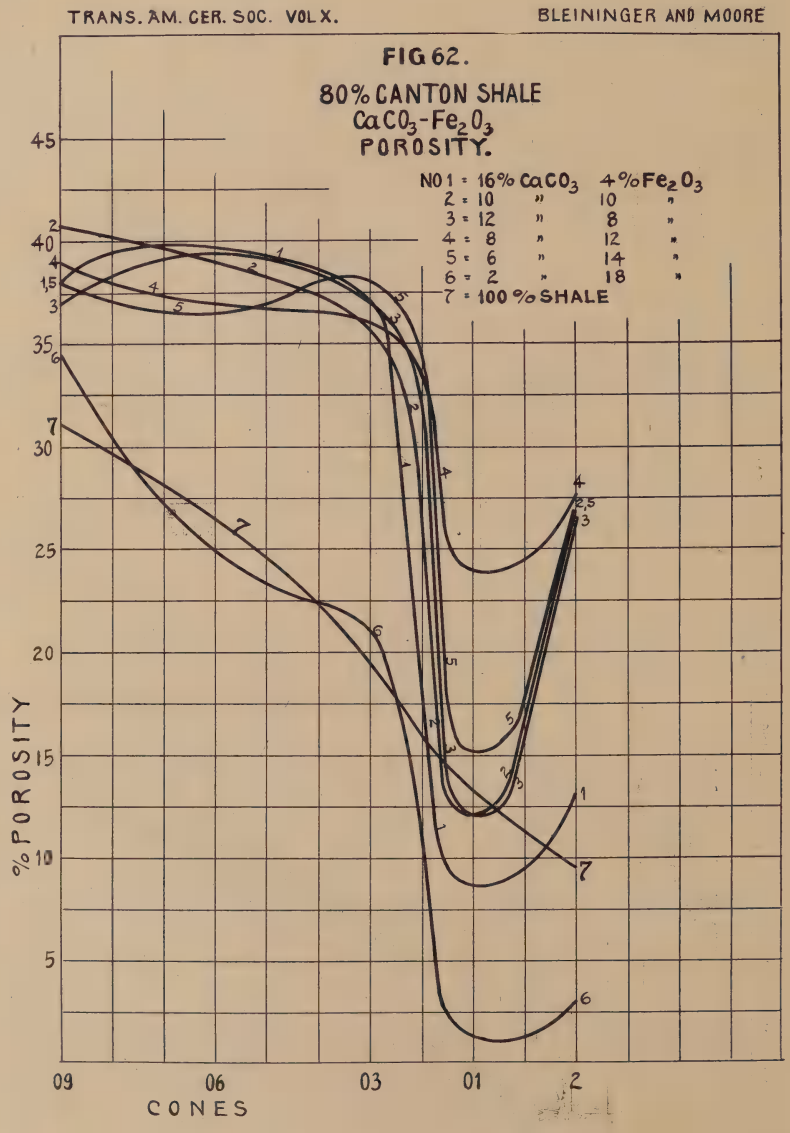
In the individual curves of the Crawfordsville shale series, Fig. 60, a gradual change in the slope of the curves is noted, which tends to become smaller as the Fe_2O_3 increases. With the increase of the ferric oxide there is observed a peculiar retardation between Cones 06 and 03, indicating perhaps some phenomena taking place between the lime and the iron. Of course it is impossible to determine just what this change is.

In the Galesburg shale series, Fig. 61, the gradation on increasing the iron is smoother and not marked by the retardation noted above, excepting perhaps in the 4% whiting, 6% Fe_2O_3 curve.

The Canton shale series, Fig. 62, is not comparable with the two preceding series, owing to the fact that here we have but 80% shale with 20% lime and iron oxide. However, some facts are brought out. First we have the change in slope with the decrease in lime, and second, we observe between Cone 01 and 2 a marked increase in poros-


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 61.
GALESBURG SHALE-$CaCO_3$-Fe_2O_3
POROSITY.
NO. 1 - 100% SHALE
2 - 90 " " 7% $CaCO_3$ 3% Fe_2O_3
3 " " " 5
4 " " " 4 6
5 " " " 3 7
6 " " " 2 8
% POROSITY
CONES
09 06 03 01 2


TRANS. AM CER SOC VOL X.
BLEININGER AND MOORE
FIG 60.
CRAWFORDSVILLE SHALE
$CaCO_3$ - Fe_2O_3
POROSITY.
NO. 1 - 90% SHALE 9% $CaCO_3$ 1% Fe_2O_3
2 " " 8 " 2 "
3 " " 7 " 3 "
4 " " 6 " 4 "
5 " " 4 " 6 "
6 " " 3 " 7 "
7 " " 2 " 8 "
8 - 100% "
% POROSITY
CONES
09 06 03 01 2


TRANS. AM. CER. SOC. VOL X.
BLEININGER AND MOORE
FIG 62.
80% CANTON SHALE
$CaCO_3$-Fe_2O_3
POROSITY.
NO 1 = 16% $CaCO_3$ 4% Fe_2O_3
2 = 10 " 10 "
3 = 12 " 8 "
4 = 8 " 12 "
5 = 6 " 14 "
6 = 2 " 18 "
7 = 100 % SHALE
% POROSITY
45
40
35
30
25
20
15
10
5
09
06
03
01
2
CONES

ity which appears in every curve, the cause of which must be sought in the production of vesicular structure. It is possible that vitrification had set in at Cone 1, in which case it was missed, since no burn was made at this temperature.

From the data presented in this paper the writers believe that the method of determining the rate of the porosity changes affords a practical means of examining the vitrification phenomena not only of natural clays, but also of body mixtures. The porosity method is essentially a practical one, and where it is desirable to know the *molecular* changes, either physical or chemical, taking place, it must be supplemented by specific gravity curves representing the true specific gravities as determined by the pycnometer, under the special precautions advised in this paper. Unless these determinations are made with great care they are of little value, since the changes involved are frequently only of small magnitudes. The specific gravity curves employed in this paper, hence, are not close enough to admit of exact conclusions.

From the scientific standpoint, therefore, wherever the discussion of the molecular structure is involved, the true specific gravity curves are the main criteria of these changes. At the same time it must be remembered that the true specific gravity is in itself the resultant of the physical and chemical phenomena clearly indicated in the first part of this contribution, and cases might occur where the rate change becomes zero, owing to neutralizing factors. These, however, seem to be the exception. The porosity curves are subject to grave errors under certain conditions.

The maximum or minimum points, so important in the study of all fusion phenomena, may frequently be detected by the porosity curves. Their determination is more exact if fixed by the specific gravity curve, since practically all physical or chemical phenomena are accompanied by a change in specific volume, and since nearly all silicates (not containing any borates) on the application of heat, as far as known, increase in volume.

The use of reagents such as have been employed in this

paper seems to the writers to be of considerable value in bringing out and studying the differences in the chemical and physical structure of clays. Different clays will respond differently to the same reagent under the same heat treatment. To illustrate, every potter knows that there is a great difference between the behavior of English china clay and American kaolins. By heating each of these clays with, say, a mixture of 20% flint and 15% feldspar to several temperatures, different porosity curves will be obtained, showing the distinct characteristic of each type of material. It goes without saying that the reagent, whatever it may be, must be kept the same, both as to composition and fineness, just as the cement manufacturers and testers employ a standard sand for their purposes. This would mean the storing of a considerable amount of such a material. The preparation of the test pieces also should be done under uniform conditions.

Another extremely important factor is the heat treatment, which should be continued long enough to establish conditions of equilibrium and should be noted as closely as possible with reference to cone temperatures. That the heating should be the same in each case is self-evident, since we know that we are dealing with incomplete reactions which differ for different heat treatments.

In this connection the need of a really satisfactory small laboratory test kiln becomes very apparent, and this problem awaits solution.

As has been said before, for practical purposes the porosity curves are amply sufficient.

There can be no doubt but that we must approach the study of our clay bodies and mixtures along this line, and before definite laws can be laid down a great deal of work must yet be done. This field has been barely opened, but it is hoped that the function of the several substances studied will be indicated. What is needed most is the study of the simpler combinations.

In conclusion, the writers wish to express their indebtedness to Professor C. W. Rolfe for having granted

the funds and facilities necessary for carrying out this work.

DISCUSSION.*

Mr. Purdy: This paper cannot be discussed at all adequately because of the mass of data presented. The curve form is probably the most lucid way of presenting data, but the mass of data is so confounding that you can not expect one to follow it in the short time which has been given it.

There were a few points though that I noticed as he went along; for instance, perhaps that iron did not seem to have acted as a flux, as we supposed it did, except in the role of a catalyzer. We noted the same thing last year in the study of the microscopic slides of burned shales, the iron separated out into definite crystals instead of combining with the silica. If iron combines with silica to any great extent it certainly would in a shale burned to a very dark chocolate color under both reducing conditions and great heat. Under each of these conditions the iron separated out into definite crystals. We have had data presented here today showing that the iron, instead of fluxing the clay, seems to have acted as a refractory agent, preventing the closing of the pores. The effect of iron on the specific gravity seems to be that to some extent. it holds it up, if it does not increase it. The same proved to be true with lime in large quantity. Lime in small quantities tends to decrease the density of clay by fusion, and hence a molecular arrangement of the fused constituent, and also by development of vesicular structure, but in excess of seven percent, it tends to increase the density of the mass. This is new to me, but I have no doubt it will be fruitful of new postulations when we come to study the curves.

It has been noted that sand added to shale increased

*This paper was not read nor presented in its entirety; such portion that was presented was given extemporaneously by Mr. Moore. Those whose discussed the paper have not had opportunity to see it as it appears above.—(Editor.)

its toughness when made into the form of brick and used as a paver. Sandy clays are as a rule better paving materials than those containing no sand; and sand—not pure quartz—added to clay increases its toughness. You cannot, however, add lake or glass sand and expect this constancy in specific gravity; nor can you expect this constancy in the porosity changes with increasing heat treatment, indicated by the curves just shown to us. You must have sand which is more or less combined, more or less in solid solution, as the chemists say, in order to have this steadiness of behavior in regard to fusion. The behavior of silica in decreasing the specific gravity without causing definite fluxing action is interesting. When a quartz crystal expands on heating it breaks, molecularly, and, at the same time, the molecules increase in volume. Notwithstanding the increased contact surface that follows as a consequence of this increase in volume, silica did not appear, in these experiments, to act as a flux.

I noticed that Cone 2 seemed to be the critical point in all mixtures, the point at which fusion begins to progress most rapidly. So Cones 2 and 3 can be said to be quite critical temperatures for most clays, if not for all clays and mixtures.

The behavior of kaolin when added to shale is most interesting. It seems to cause a fluxing action in small amounts and a refractory action in larger amounts. What is a flux? We have been used to classifying the bases, lime, magnesia, etc., as fluxes. We classify Cornwall stone and feldspar as fluxes, and clay and sand as refractories. We have an instance here of clay, a very refractory material, acting as a flux when mixed with shale. How can we harmonize this with our definition of a flux? It seems we ought to have a different definition from that we have been using.

PYRO-PHYSICAL BEHAVIOR OF FLINT FIRE CLAYS.

BY

Ross C. Purdy, Columbus, Ohio.

The investigation of the pyro-physical behavior of clays reported to this society last year by Mr Moore and myself is an illustration of a fact, to-wit, that no single research, even though comparatively broad and thorough, can be said to be exhaustive or complete. In a laboratory course in Ceramics at the Ohio State University, under the direction of Prof. Orton, students made porosity and specific gravity determinations on burned brickettes by the method described by Mr. Moore and myself. In all instances, aside from the flint fire clays, there was a close agreement to the findings reported last year. These exceptional cases constituted evidence which is not contradictory to the observations previously reported but rather, as will be seen, adds to and broadens our general considerations of pyro-physical behavior of clays.

No description of methods of testing or conditions attending the same need be given, except that the plan of procedure described last year was faithfully followed in detail, and that students worked in pairs. While two students worked together on the preparation, burning and testing of the brickettes, the calculations and reports were prepared by each student independently. The tests here reported were the third of the same kind which the students made, hence considerable reliance can be placed upon the accuracy and general quality of their work.

The clays which differed in pyro-physical behavior from those described last year were:

(1) Olive Hill Flint Fire Clay, tested by A. T. Malm and K. Takahaski.

(2) Mineral City Flint Fire Clay, tested by J. D. Whitmer and J. M. Knote.

(3) Jackson County Flint Fire Clay, tested by C. R. Cooper and H. E. Coran.

(4) Portsmouth Flint Fire Clay, tested by W. H. Dittoe and W. H. Artz.

OLIVE HILL FLINT FIRE CLAY.

This is a characteristically grey-colored, hard flint clay with conchoidal fracture, not plastic when dry ground and having but very little plasticity when wet ground. Drying shrinkage averaged 3.2%.

PROPERTIES WHEN BURNED.

Hardness. Brickettes drawn prior to receiving Cone 08 heat treatment were easily crumbled with the fingers. Progressively increased hardness, however, was obtained with increased heat treatment until at Cone 10 they resisted knife scratching fairly well.

Shrinkage. Up to Cone 010 the fire shrinkage increased to 4%, but from Cone 010 to Cone 1 there was an increase of only 1%, making a total of 5% at Cone 1. From Cone 1 to Cone 11 the fire shrinkage increased quite steadily from 5 to 9%.

Figure 1 shows the fire shrinkage in curve form.

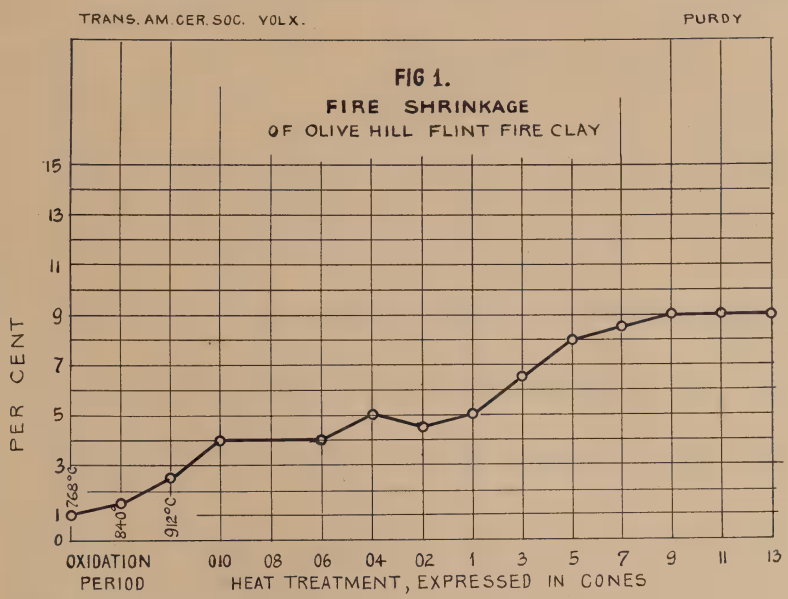
Porosity and Speific Gravity Changes. In figures[1] 2 and 3 are shown the porosity and specific gravity changes produced by various intensities of heat treatment. The porosity changes are what would be expected from a No. 1 fire clay. The steady, even though slight, increase in specific gravity of the solid material[2] in the brickettes from Cone 010 to 10 instead of a decrease as noted in the plastic No. 1 fire clays reported last year, is noteworthy.

Without attempting to discuss the curves in figures 1, 2 and 3, the data were recasted[3] into terms of volumes, as will be explained. The aim in recasting the usual linear data was to be able to combine them on a volume chart,

[1]Drawn by the students who made the tests.

[2]The specific gravity here referred to is that of the portion of a saturated brickette not occupied by the water.

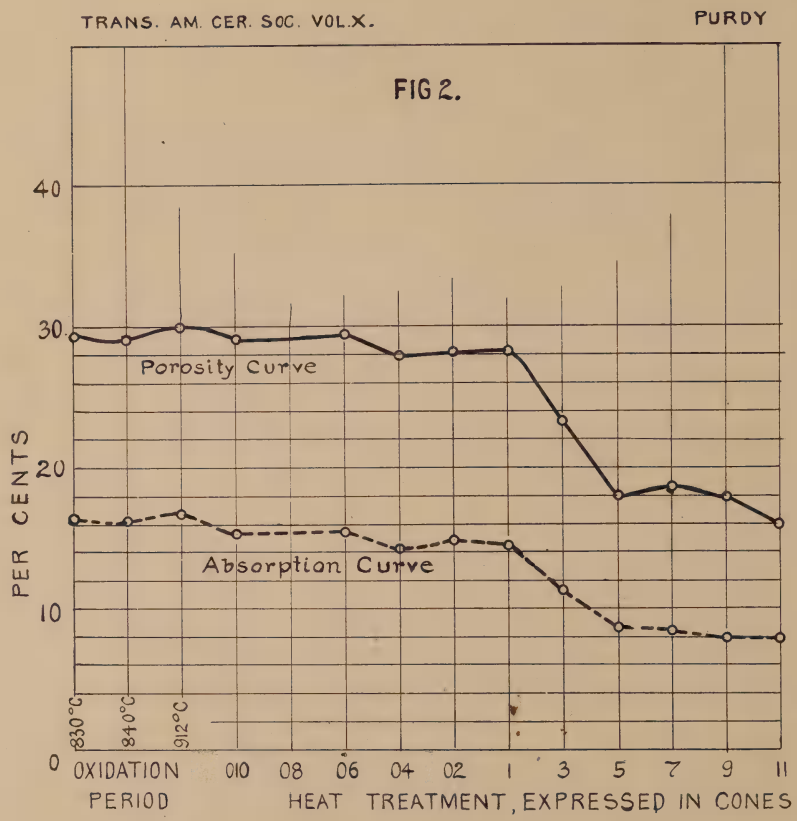
[3]By the present writer.



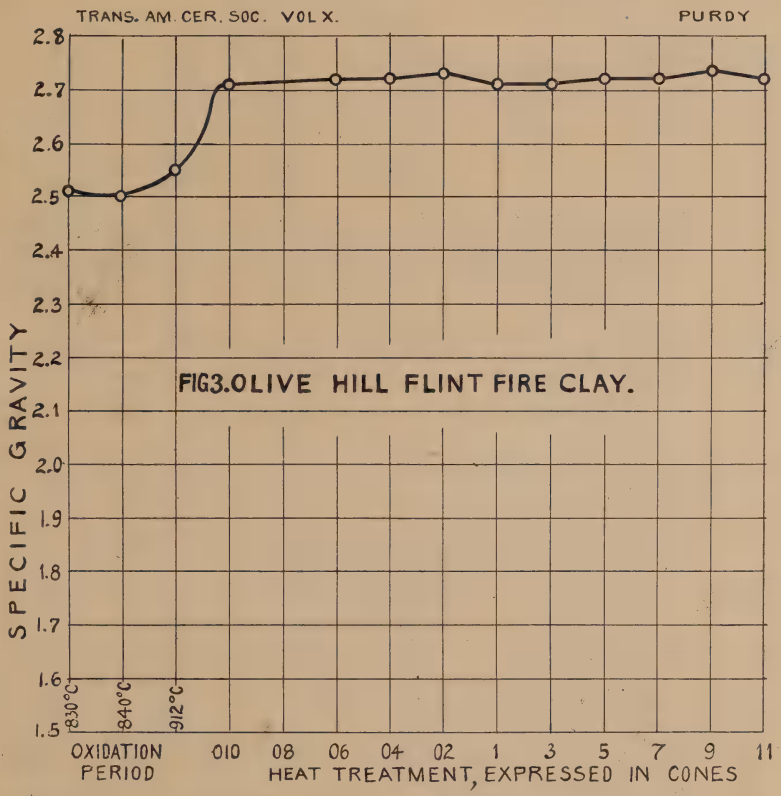
thus showing more clearly the significance of the changes induced by increasing intensity of heat treatment.

Since we have not the true specific gravity of the solid material in the brickettes, it will be impossible to show the volume of the vesicular pores. If such data were at hand the volume of the vesicular pores relative to the volume of the impervious solid portion of the brickette could be calculated by the formula $\left(\frac{T-A}{T}\right)(I—P)$ where T is the true and A the aparent specific gravity, and P the volume of open pores per unit volume of brickette.

In order to show the cubical shrinkage suffered by each brickette it is necessary to have the volume of the brickette just prior to burning, i. e., when in the dry unburned condition. Such data are not at hand, but since we have the saturated and suspended weights in each case, we can calculate their volume when burned and then, with the shrinkage data, calculate back to the dry unburned volumes. This necessitates the conversion of the linear into cubical shrinkage.



If we had a cube of a solid, of which the coefficient of linear shrinkage was "a," and each edge of which measured 1 centimeter, the length of each edge would become, after shrinking, 1—a; hence the volume would become $(1—a)^3$ or $1—3a+3a^2—a^3$. Since the original volume equaled unity, the amount of cubical shrinkage per unit volume or, as it is known, the coefficient of volume shrinkage, would be $3a—3a^2+3a^3$. Therefore if the shrinkage per 100 units linear length is 3.2, the amount of shrinkage per unit length would be 3.2-100dts. or 0.032 units. This converted to cubical shrinkage would be, according to the above formula



$3(.032) - 3(.032)^2 + (.032)^3$ or $0.096 - 0.00306 + .00003$[1], which is equal to 0.093, or in terms of percents, 9.3.

The percentage cubical fire shrinkage as calculated from the linear data for this clay is given in column 8 of the following table.

If F is the cubical fire shrinkage per unit volume, the dry unburned volume would be (W—S) (1+F) where W and S are respectively the saturated and suspended weights of the burned brickettes. Results of such calculations are shown in the ninth column of the following table:

[1]It is obvious that when the value of "a" is small the third term in this conversion formula may be omitted. The second term ($3a^2$) however should never be omitted. This last statement is at variance with opinion of W. Jackson. (Text Book on Ceramic Calculations, p. 5.)

TABLE I.

Data Obtained on Burned Brickettes made from Olive Hill Flint Fire Clay.

1 No.	2 Cone	3 Dry Wt.	4 Sat. Wt.	5 Sus. Wt.	6 Apparent Specific Gravity	7 % Porosity	8 % Linear Fire Shrink	9 Calulated % Cubical Fire Shrink	10 Calculated Volume of Uuburned Bricketts
1	...	44.68	51.96	26.78	2.50	28.91	1.0	2.97	25.93
2	...	37.14	43.24	22.40	2.52	29.27	2.0	5.88	22.07
3	...	41.02	47.71	24.64	2.50	29.00	1.5	4.43	24.08
4	...	44.10	51.49	26.80	2.55	29.93	2.5	7.31	26.49
5	010	39.57	45.59	24.98	2.71	29.21	4.0	11.52	22.97
6	06	42.02	48.54	26.55	2.71	29.65	4.0	11.52	24.52
7	04	35.43	40.51	22.39	2.72	28.04	5.0	14.25	20.66
8	02	36.18	41.57	22.94	2.73	28.93	4.5	13.30+	21.04
9	1	39.82	45.64	25.14	2.71	28.39	5.0	14.25	23.37
10	3	38.05	42.40	24.00	2.71	23.64	6.5	18.33	21.71
11	5	40.97	44.53	24.91	2.71	18.15	8.0	22.08	23.94
12	7	42.99	46.66	27.16	2.72	18.82	8.5	23.33	23.98
13	9	47.41	51.20	30.12	2.74	17.98	9.0	24.57	26.16
14	11	32.99	35.55	20.91	2.73	17.49	9.0	24.57	18.14
15	13	41.74	44.87	26.51	2.74	17.05	9.5	25.79	23.13
16	13	30.05	32.36	19.08	2.74	17.39	9.0	24.57	16.6

Having thus calculated the dry unburned volume (V), the volume data can now be reduced to parts of 100 unit volumes of dry unburned brickette by multiplying each by the factor $\frac{100}{V}$. Data given in columns 4, 5 and 6, of the following table, were so calculated. Data in columns 5 and 6 should, when added together, equal the data given in column 4.[1]

In column 7 is shown the cubical shrinkage data calculated as before described. If the brickettes had been completely saturated so as to have correct volume data for the open pore and impermeable solid, data in columns 5, 6 and 7 should total 100. In column 8 is given the totals obtained in this experiment. It will be noted that the error increases as the brickettes become less porous. The less porous the brick the more difficult is it to obtain com-

[1]This is obvious from the equation (D—S)+(W—D)=W—S. Slight variance from this as shown in the table is due to error incident to slide rule calculations.

plete saturation, and the difference between the totals given (column 8) and 100 is considered as a measure of the incompleteness of saturation.

TABLE II.

Showing (4) volume of burned brickette; (5) volume of impervious solid portion; (6) volume of open pores; in terms of 100 volumes of dry unburned brickettes.

1 No.	2 Heat Treatments	3 Value of $\frac{100}{V}$	4 Volume of Burned Brickettes $(W-S)\left(\frac{100}{V}\right)$	5 Volume of Impervious Solid $(D-S)\left(\frac{100}{V}\right)$	6 Volume of the Open Pores $(W-D)\left(\frac{100}{V}\right)$	7 Cubical Shrinkage	8 Sum of Data in Columns 5, 6 and 7
1	760°C	3.86	97.5	69.0	28.1	2.97	100.07
2	830°C	4.54	94.5	67.0	27.7	5.88	100.6
3	840°C	4.15	96.0	68.0	27.7	4.43	100.1
4	912°C	3.78	93.4	65.2	28.0	7.31	100.5
	cone						
5	010	4.36	90.2	63.8	26.4	11.52	101.7
6	06	4.07	89.5	63.0	26.6	11.52	101.1
7	04	4.85	88.0	63.5	24.6	14.25	102.4
8	02	4.75	88.5	63.0	25.6	13.30	101.9
9	1	4.3	88.1	63.1	25.0	14.25	102.4
10	3	4.6	84.5	64.8	20.0	18.33	103.1
11	5	4.18	82.1	67.0	14.9	22.08	104.0
12	7	4.17	81.5	66.0	15.0	23.33	104.0
13	9	3.83	81.0	66.0	14.5	24.57	105.1
14	11	5.5	80.8	66.5	14.1	24.57	105.2
15	13	4.3	78.8	65.8	13.2	25.79	104.8
16	13	6.05	80.5	66.5	14.0	24.57	104.6

The volume values given in Table II are shown graphically in Figure 4. The ordinates are parts per 100 unit volumes of the brickettes prior to burning, and the abscissae are heat treatment.[1]

[1]The full ordinate length AC=volume of dry unburned brickette.

Ordinate lengths FC and ID=to volumes of impervious solid in burned brickettes.

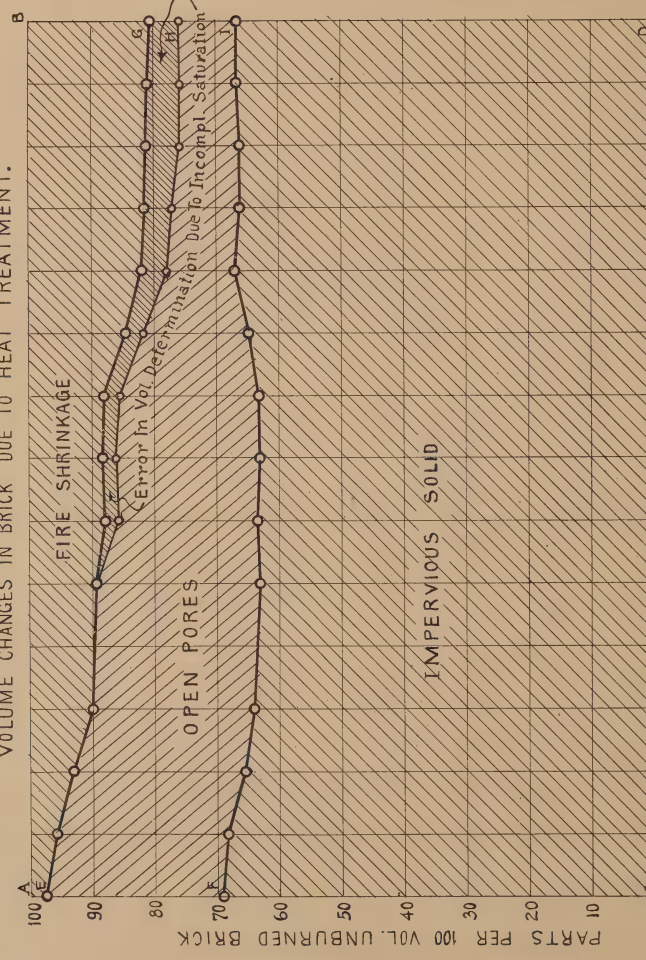
Ordinate lengths EF and GI=to volumes of open pores in burned brickettes.

Ordinate lengths AE and BG=cubical fire shrinkage.

Ordinate length GH=error introduced by incomplete saturation, etc.

FIG 4. **OLIVE HILL FLINT FIRE CLAY,**

VOLUME CHANGES IN BRICK DUE TO HEAT TREATMENT.



Since the ordinate distances between the curves shown on the chart are equivalent respectively to the volumes of the impervious solid, open pores and loss due to shrinkage, the simultaneous volume changes due to increasing heat treatment can be readily followed.

PORTSMOUTH FLINT FIRE CLAY.

No.	Cone	Dry Weight	Sat. Weight	Sus. Weight	Specific Gravity	% Porosity	Linear Fire Shrinkage	Calculated % Cubical Fire Shrinkage	Calcult'd Volume of Unb'rne1 Brickett's
1	760	54.66	63.00	32.10	2.42	26.99	2.22	6.45	33.0
2	830	54.05	61.12	31.55	2.40	23.91	2.22	6.45	31.6
3	840	63.20	72.65	37.49	2.46	26.88	2.22	6.45	37.5
4	912	53.55	61.48	31.97	2.48	26.87	2.78	8.10	31.9
5	010	56.73	65.59	35.12	2.63	29.07	4.44	12.60	34.2
6	06	56.22	64.65	35.19	2.67	28.61	5.00	14.25	33.8
7	04	55.92	64.02	35.08	2.68	27.98	5.00	14.25	33.1
8	02	56.69	64.95	35.56	2.68	28.10	5.00	14.25	34.6
9	1	68.52	78.30	43.25	2.71	27.90	5.00	14.25	40.5
10	3	65.16	73.45	40.58	2.65	25.22	6.11	17.18	38.5
11	5	43.19	47.67	26.66	2.61	21.32	7.50	20.04	25.3
12	7	56.50	61.85	35.24	2.66	20.10	8.12	22.38	32.5
13	9	39.31	42.86	24.72	2.69	19.57	8.75	23.95	22.5
14	11	63.70	69.05	40.09	2.70	18.47	8.75	23.95	35.9
15	14	46.45	50.51	29.19	2.69	19.04	8.75	23.95	26.4
16	14	41.83	45.48	26.03	2.65	18.76	8.75	23.95	24.2

Data and curves for the Portsmouth Flint Fire Clay are also presented. From the curves and volume chart it is plain that these two flint fire clays have pyro-physical properties that are very much alike. Indeed, the same is true for all the four flint clays tested, making introduction of their data superfluous.

The most important fact to be noted from these volume charts is that, notwithstanding that there is a slight increase, rather than decrease, in specific gravity from Cone 1 to 11, there is an actual swelling of the impermeable solid portion. This increase in volume of the solid portion was noted in every clay reported last year. In those clays and all other clays since tested there was accompanying this swelling of the solid portion, a very decided decrease

in specific gravity. Why, in the flint fire clays there is an increase in specific gravity coincident with increase in volume of the impermeable solid portion, rather than a decrease, is only one more puzzling phenomenon added to the already long list of peculiarities of this clay.

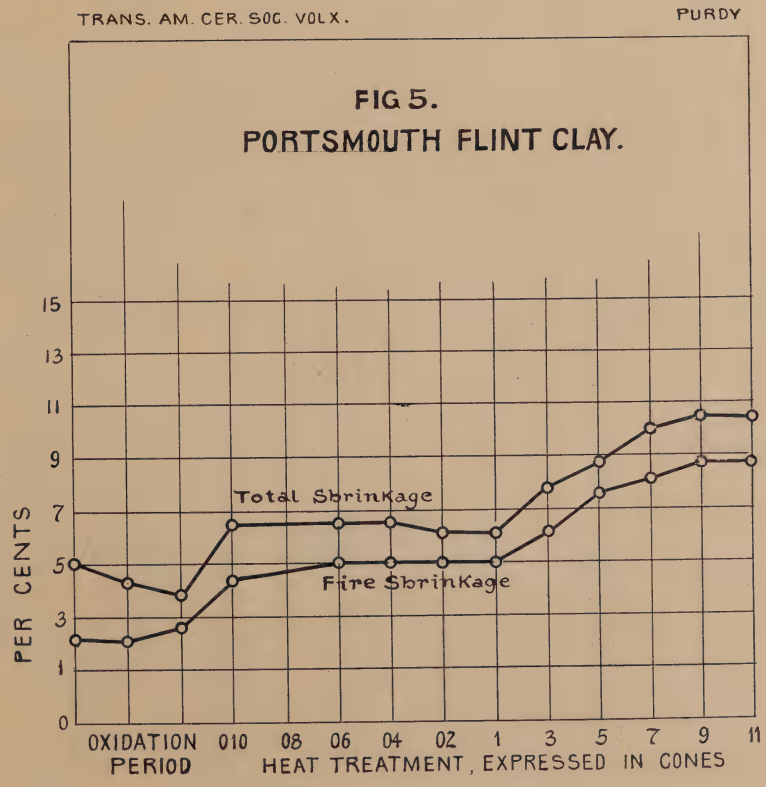
PORTSMOUTH FLINT FIRE CLAY.

1 No.	2 Cone	3 Value of $\frac{100}{V}$	4 Burned Brickette $(W-S)\left(\frac{100}{V}\right)$	5 Imperious Solid $(D-S)\left(\frac{100}{V}\right)$	6 Open Pores $(W-D)\left(\frac{100}{V}\right)$	7 Cubical Shrinkage	8 Sue of data in columns 5-6-7
1	760	3.03	94.0	68.6	25.6	6.45	100.6
2	830	3.18	94.0	71.3	22.5	6.45	100.3
3	840	2.67	94.0	68.7	25.3	6.45	100.4
4	912	3.15	93.0	68.3	25.0	8.10	101.4
5	010	2.93	89.0	63.6	26.0	12.60	102.2
6	06	2.96	87.3	62.1	25.0	14.25	101.4
7	04	3.03	87.3	63.0	24.0	14.25	101.3
8	02	2.98	87.3	63.3	24.6	14.25	102.2
9	1	2.46	87.3	62.3	24.3	14.25	100.9
10	3	2.60	85.3	63.0	21.5	17.18	102.7
11	5	3.95	83.0	65.2	17.5	20.04	102.7
12	7	3.08	82.0	65.8	16.5	22.38	104.7
13	9	4.45	81.0	64.9	15.8	23.95	104.7
14	11	2.80	81.0	66.0	15.0	23.95	104.9
15	14	3.80	81.0	65.7	15.4	23.95	107.0
16	14	4.14	81.0	65.5	15.1	23.95	104.5

The fact also that the flint fire clays do not behave differently from other highly refractory clays, in that they show evidence of fusion at about Cone 3 with an attending swelling of the solid portion of the brick, is taken that this type of clay differs from other types only in the matter of their unexplainable increase in specific gravity.

As previously stated, the true specific gravity of the burned material was not determined, hence statements cannot be made concerning the physical changes (in consequent fusion) which caused the increase in volume of the solid portion of the brick. If formation of blcb structure was the sole cause, there should have been a de-

crease in apparent density. If the observed increase in apparent density was due to molecular condensation, then we should have had a decrease in volume. Let me ask, therefore, in closing, have we in flint fire clays a case where, if bleb structure were not developed, there would be an enormous (i. e., very extraordinary) increase in density due to molecular condensation; and, in the case above cited, is the swelling of the body, due to bleb structure sufficient to counteract the affect of molecular condensation volumetrically but not gravimetrically? It will be of interest in such cases to have true specific gravity data in conjunction with the apparent specific gravity and volume data.



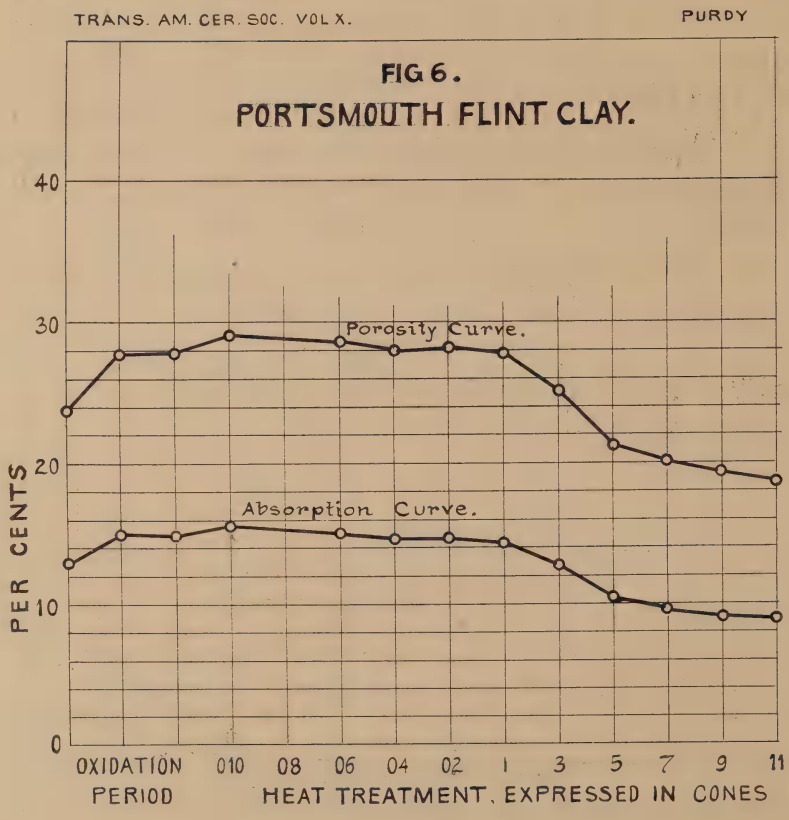
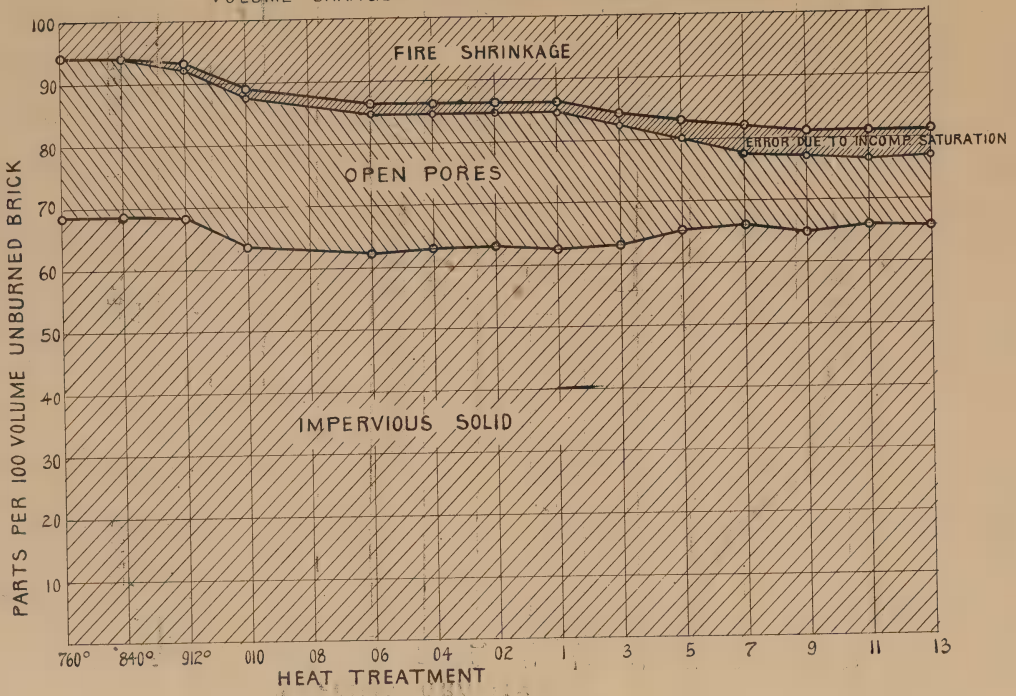

TRANS. AM. CER. SOC. VOL X.
PURDY
FIG 6.
PORTSMOUTH FLINT CLAY.
Porosity Curve.
Absorption Curve.
PER CENTS
0
10
20
30
40
OXIDATION PERIOD
010
08
06
04
02
1
3
5
7
9
11
HEAT TREATMENT, EXPRESSED IN CONES

FIG 7. PORTSMOUTH FLINT FIRE CLAY.

VOLUME CHANGES IN BRICK DUE TO HEAT TREATMENT



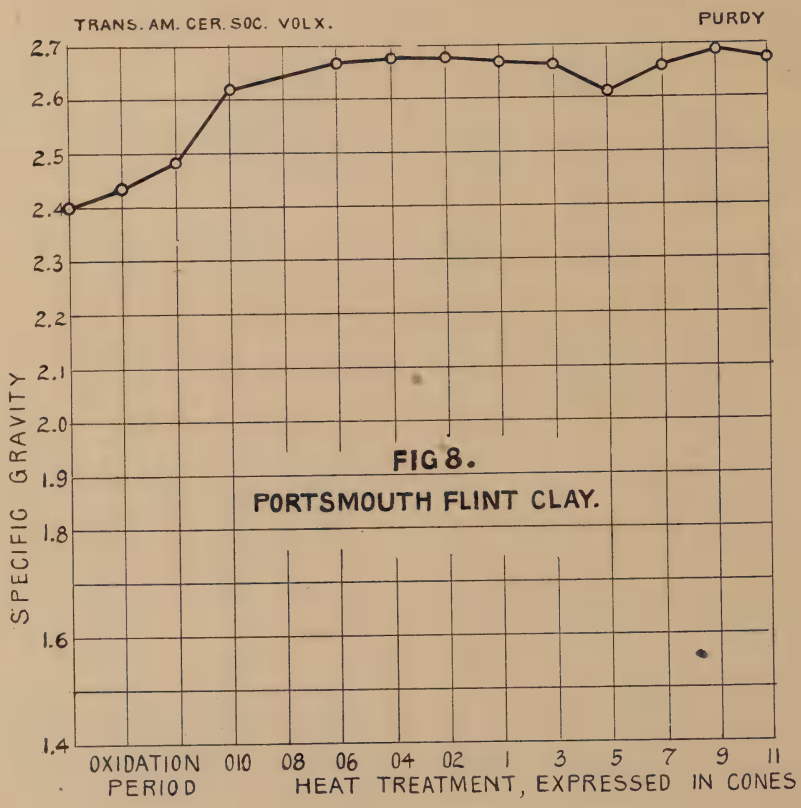


FIG 8.

PORTSMOUTH FLINT CLAY.

DISCUSSION.

The Chair: This paper is open for discussion, and we would like to hear it quite fully discussed. Of course, it is a comparatively new field, yet old. The fact has been known but it has never been used like Mr. Purdy used it, and it seems to me a very important field. There is no question but that we must know more about those reactions which are taking place during vitrification, and this is one of the most valuable ways of getting at it.

Mr. Burt: Is this series based on wet ground or dry ground series?

Mr. Purdy: These were flint fire clays, and they had to be wet ground in order to be formed into brickettes.

Mr. Knote: We tried at first to dry-grind the clays. The problem was to work it up into brickettes on which the shrinkage and other properties could be measured. It was put in a wet pan and ground until it was possible to shape it up into brickettes of the desired shape. The average time it was wet-ground was about half an hour. Some were ground less and some more.

The Chair: Can you give us your ideas about the peculiar phenomena observed here?

Mr. Knote: I have not had an opportunity to make a detailed study of the subject. We all know from Professor Purdy's bulletin from the University of Illinois that the specific gravity went down as the mass got smaller or shrank. But in this case, although it did shrink, the specific gravity went up. We assumed in the plastic fire clays that a vesicular structure had been formed. In this case it had passed through the vitrification stage without vesicular structure having been formed.

The Chair: We found in recent experiments, on adding ferric oxide to the clay we got peculiar conditions—got a condensation where we did not expect it.

THE ARRANGEMENT OF MANUFACTURING AND SELLING COSTS.

BY

ELLIS D. GATES, Seattle, Wash.

Many times have I recalled the statement made in 1899 by our worthy instructor, Professor Edward Orton, Jr., "The ceramic lines are in the same relative position that the steel business occupied twenty years ago," and observed how true thus prophecy was proving. But to attain the position in question we must do as the steel men have done; namely, make our products better and cheaper, therebymaking them more desirable to the consumer and enlarging the market for them.

This we are accomplishing by a better knowledge of ceramics and the growing market for the various clay products. But the accounting has been done in many instances in a haphazard way, which in other lines would have been suicidal.

The changes in business in the last decade have made a reliable Cost System a necessity. The various ceramic lines in common with all lines of manufacturing business have been, as it were, between two mill stones—higher wages and higher cost of both raw and finished materials on one side, with lower selling prices on the other, making it imperative that the actual cost of production be known, and making the space between the two sides, which represents cost and profit, smaller each year. Thus if a business is to be run at a profit the cost of production must be lowered. This can only be accomplished by having carefully compiled figures arranged to give the information desired. A firm having no record of costs only knows at the end of their fiscal year that they have made or lost money, but cannot tell where, or how or when.

Figures taken as a whole do not tell much unless properly arranged and compared, and if costs are to be reduced it is necessary that they be so subdivided that the owner, manager or superintendent can tell at a glance which are increasing and which ones are most likely fields for careful, systematic study for the purpose of reduction of costs.

Some cost systems fail in that they do not go into detail enough, and therefore do not show the exact point of the leak, which will in all probability be easily stopped once it is located. In arranging the following system the writer has gone into only enough detail to show the cost in each operation or department. His experience since entering actively into the ceramic line has been mostly on the business side, and he has therefore given more attention to managment than to ceramics proper. He hopes that the system outlined here will be of some aid in lifting the clay working lines to their proper place in business, and in leading to a better understanding of the collection and arrangement of figures and costs.

This system has been in operation the past year with good results, in a terra cotta plant, but as the basic principles of all lines of business are identical, it can be adapted to almost any manufacturing business. In using this system a unit of measure must be decided upon, on which the cost can be determined. This unit may be cubit foot, ton, dollar value, or a certain number of the article manufactured.

Many firms take the production per month of one department and use that as a basis in calculating the cost in other departments. This is obviously wrong, as some other department may produce twice as much in the month as the department selected as a basis. In this system I therefore calculate the cost in each department by using the number of units actually processed in that department, each week or month, and the result is therefore actual and accurate.

Chart No. 1* is the form used for the final cost sheet, omitting of course, the explanatory diagram at the left side of the sheet.

CHART I.

			Department	Month				Month			
				Cubic Feet	Cost	Cost per cu. ft.	%	Cubic Feet	Cost	Cost per cu. ft.	%
TOTAL COST			Clay								
			Plaster								
			Kiln Fuel								
			Slips								
			Other Supplies								
			Total Material								
			Draughting								
			Models & Moulds								
			Modeling								
			Clay Mixing								
			Pressing								
			Cutting								
			Drying								
			Slipping								
			Setting								
			Drawing								
			Burning								
			Fitting								
			Shipping								
			Direct Labor								
			Total Labor								
			Total Prime								
			Upkeep								
			Power—Heat								
			Rent & Taxes								
			Insurance								
			Depreciation								
			Indirect Labor								
			Total Burden								
			Total Factory								
			Office								
			Salesmen								
			Estimates								
			Advertising								
			Stationery								
			Traveling								
			Freight								
			Indirect Exp.								
			Total Selling								
			Total Cost								

*For reference see A. H. Revell in "Cost of Production."

The first division, as you will note, divides the Total Cost into Factory Cost and Selling Cost, which must be considered separately, as each is independent of the other.

Factory Cost. Factory Cost is composed of Prime Cost and Burden, which must be kept distinct, as Prime represents the necessary expenses of material and labor, while Burden covers those which go to make up the "load" or "burden" a business has to carry.

Prime Cost. The divisions of Material and Labor under Prime are easily decided upon, as Material covers all clay, coals to kilns (but not for boilers, which should be placed under Burden) and supplies of all kinds. The cost of the materials may include labor necessary to place the material in the store house or bunker, or to unload, but it is better practice to consider that under Indirect Labor, so that these costs may be kept down to the minimum.

Labor. Labor should include all labor in different departments or operations through which the product passes—the more it is subdivided the better one can see where the costs increase or decrease from month to month.

On point requiring special stress is the distribution of Direct Labor and Indirect Labor—one being found under Labor and one under Burden. Most authorities define them about as follows:

Direct Labor is all labor which has to do with actually processing the material itself.

Indirect Labor is labor which does not directly process material and is therefore chargeable to Burden, under one or more of its subheads. You will readily see that Indirect Labor must be given a close and careful scrutiny, as it is a great factor in increased costs.

The total of Material Cost and Labor Cost make up Prime Cost.

Burden. Burden covers Upkeep or Repairs, Power, Heat, Light, Etc., Rent and Taxes on plant, Insurance, Depreciation and Indirect Labor, which last may be subdivided for different kinds of indirect labor.

All of these items represent "Overhead Expenses,"

"Fixed Charges" or "Gravestones," as they are variously called, and all need to be kept at the lowest possible point. The arrangement permits of their being considered alone, which is of itself a great aid in cost lowering.

The total of Prime Cost and Burden shows the Factory Cost.

Selling Expense. Selling expense is the last but fully as important as any. It should cover all expenses of the business outside Factory Expenses, and should be subdivided into enough departments or parts to give the desired information about the selling expenses. For example, Office, Stationery, Printing, Salesmen, Estimates, Advertising, Traveling, Freight, Legal, Etc.

The total of Factory Cost and Selling Cost give total cost, and fixes the price below which you cannot go without losing money. When a competitor sells goods below your Total Cost you may be sure that he is either doing business at a loss, or has better methods and lower costs than you have, leaving it for you to investigate and lower your own costs if possible.

This will explain Chart I fully I believe.

If the proper unit is selected, the system carefully followed and adapted to the individual business, and care used to assure reliable records (not estimates) of production, any man may have the exact cost in each part of his business, thereby knowing what he can do and what he cannot do, avoiding loss and keeping the efficiency of his plant and business up to the highest possible point.

The charts numbered two, three and four are some of those used in compiling the costs in a terra cotta plant. They can easily be worked out for any line of business and arranged so that they will give the daily or wekly report of production in each department. I believe a few words will explain the use of each and show the method followed.

The unit selected in this particular case was a cubic foot.

Chart No. 2 is the Distribution Sheet. One of these is made up daily and is a summary of the Daily Reports

CHART II.

Distribution Sheet for.....19....

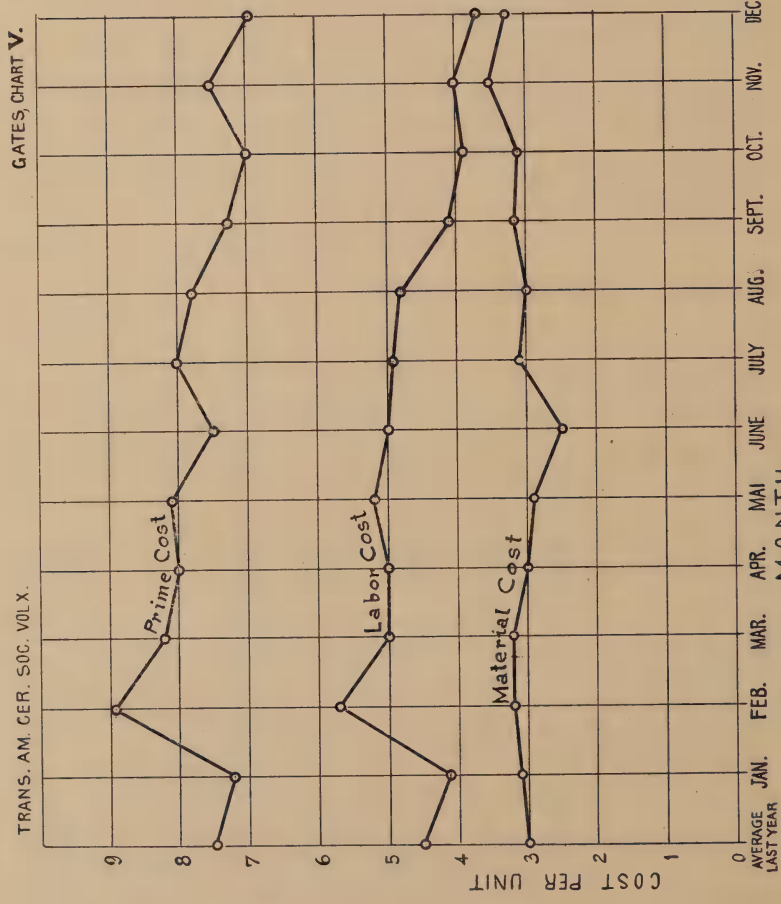
No.	Rate	Hrs.	Total	Clay Mixing		Kiln Fuel		Draughting		Models & Mou	
				Cu. ft.	Cost	Cu. ft.	Cost	Cu. ft.	Cost	Cu. ft.	Cos
1											
2											
3											
4											

(SHOWING LEFT END OF SHEET)

and time cards arranged by departments. These are in turn summarized for the month on a similar sheet and the monthly totals transferred to the Cost Sheet (Chart 1), and the cost per unit calculated.

After the cost per unit is found the percentage of each Unit Cost and Total Cost is calculated, taking the Total Cost as 100%. This gives an entirely different figure and serves as a check on corresponding departments for different months, as for example, the Department of Pressing is 5% of the total in April while it was 6% in March. The percent may also be calculated on the basis of the Total Cost in Material, Labor or Burden, or Total Factory Cost may be used as 100% in all departments under that heading, and Total Selling Cost be used as the basis for all selling cost departments. The figures thus accumulated are easily obtained, and while they show much in one month they become more valuable as they increase in number, and being systematically arranged, they show actual results from which detailed information can be obtained.

By charting these figures as shown on Chart No. V, a manager or superintendent can have daily or weekly infor-


GATES, CHART V.
TRANS. AM. CER. SOC. VOL X.
Prime Cost
Labor Cost
Material Cost
COST PER UNIT
0
1
2
3
4
5
6
7
8
9
AVERAGE LAST YEAR
JAN.
FEB.
MAR.
APR.
MAI
JUNE
JULY
AUG.
SEPT.
OCT.
NOV.
DEC.
MONTH

mation before him, and see at a glance exactly how the business is running.

This method of illustrating figures is rapidly growing in use, and once used it is sure to be adopted, as all sorts of information can be charted, and curves made which will show instantly the comparisons needed without having to note the exact figures.

CHART III.

Daily Setting Report.

Kiln No..... Date Set .....
Page No..... Amt. of Kiln Filled.....

Order No.	Mark	Pieces Set.	Total Pcs.	Total cu. ft.

Slip used.

Galls.....					
Order					
Cost					

Total Cu. Ft.

Total Forwarded .....

Total in Kiln

Percent of Kiln Filled.....

.....

Foreman.

Hrs. Today
Hrs. Ford.....
Total Hrs.

CHART IV.

Daily Plaster Shop Report.

Date.....

Plaster Used	Iron Used	Templates Made	Moulds Completed Order No.	Mark	For Pcs.	Total cu. ft.

No. Men.....

No. Hrs.....

.....

Foreman.

In conclusion the writer wishes to say that this system represents much work and study on his part, and he only hopes that it may prove of some use to another struggling clay worker, and serve to bring out other opinions and experiences in this much needed branch of the clay business.

While this system may appear difficult to handle at first you will be surprised to find how easily all the figures can be obtained. The writer in using it in a terra cotta plant, which is about as difficult as business to systematize as one could imagine, found that he could keep the reports figured up himself without interfering with his regular duties.

This system is not wholly original but is the adaption of several systems used in different lines, taking the best features from each, and arranging them in such a manner that they will yield the greatest possible amount of information.

THE VISCOSITY OF CLAY SLIPS.

BY

A. V. BLEININGER, Champaign, Illinois.

The plasticity of clays is still a quality whose physical definition has not yet been established, though many attempts have been made to do so. All we can do at present is to continue the search for some criterion which bears some relation to this elusive property. Up to the present such properties of the clay as the tensile strength, both green and dry, its deformation, crushing strength in the green state, and also recently the viscosity imparted to suspensions of clay particles have been studied. This last property is promising inasmuch as it produces a phenomenon which is clearly not shared by non-plastic materials. *In fact, it might be said that clays are rocks which when pulverized and suspended in water produce a decided increase in viscosity.*[1]

This viscosity is capable of being expressed numerically with a degree of accuracy which is superior to that of any of the methods mentioned above.

Simonis[1] has measured the viscosity by determining the volume of a clay-slip flowing through an aperture of 2 mm., under constant pressure, in a given time. A mariotte flask was used to maintain constant pressure in the burette containing the slip. The burette was first standardized with water and the relation existing between the volume flowing from the tube and the pressure obtained. This relation is evidently v=kp, where v=volume of liquid discharged in a given time, p=pressure of the liquid or its height in the vessel, and k=coefficient of fluidity or the viscosity. Solving for k we obtain $k=\frac{v}{p}$ If now the pressures are plotted along the abscissa and the volumes es-

[1]Sprechsaal, 1905, 597.

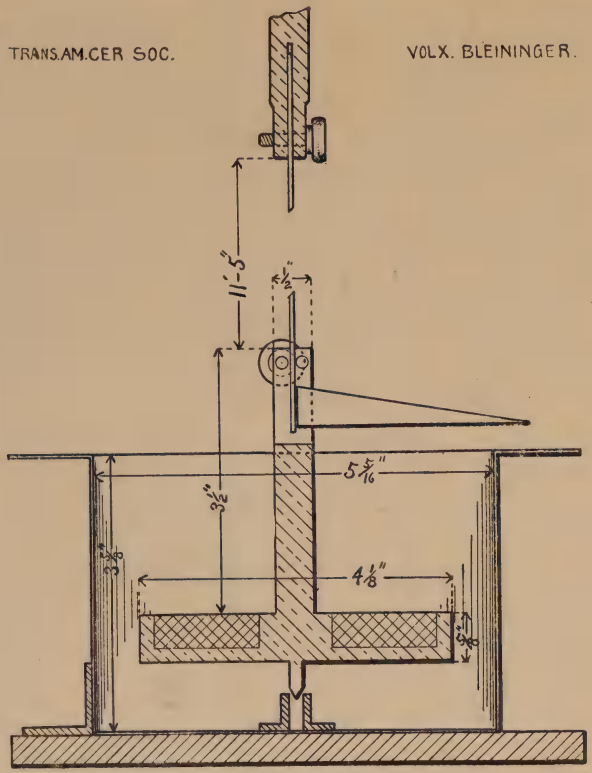
caping, along the ordinate we obtain for ideal liquids straight lines where $\frac{dv}{dp}$ is equal to the coefficient of fluidity represented by the tangent of the angle made by the line to the x axis.

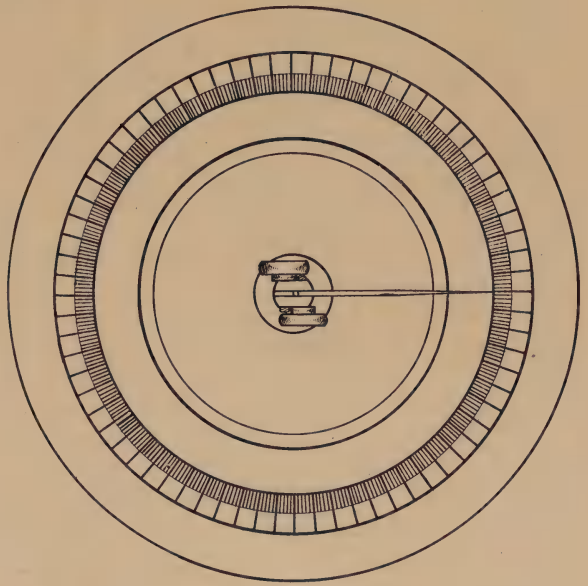
In the case of clay slips Simonis found the relation to be not so simple and he obtained as the functions of volume and pressure, curves of higher degree. The same investigator, having found considerable difficulty with this method in working thick slips, devised a second method for determining the cohesion of clay slips by measuring the weight necessary to pull away a 5 cm. glass plate from the surface of the liquid. For this purpose he arranged a balance, having the glass disc attached at one end of the beam and a scale pan at the other. He caused very fine shot to pour onto the pan, arranging at the same time an automatic shut-off device. Before working with clay slips he determined the weight necessary to pull away the disc from water. Applying the test to clay suspensions and noting the weight necessary to release the disc he subtracted from this load the weight required to pull away the glass from water, which is a constant factor. In this way the cohesion value of the clay for the concentration employed was determined. This method is applicable to thick slips which fail to give results by the flow method.

There are faults inherent with both of these methods, the flow method being subject to irregularities caused by the roughening of the walls of the vessel, the irregular stopping up of the aperture and other difficulties while the disc method is faulty as soon as even the slightest settling takes place.

In looking about for a method which perhaps might overcome some of these difficulties the Coulomb method, as employed in the determination of the viscosity of oils, was considered and adopted. Although the apparatus as designed is not suitable for thick slips, some interesting results were obtained, and the ease and accuracy with which the viscosity of thin slips could be determined makes

TRANS. AM. CER. SOC. VOL X. BLEININGER.





Viscosity Apparatus.

Fig. 1.

it quite suitable for certain investigations. It has afforded the writer a delicate means of distinguishing clays of different plasticity, or of following the effects of electrolytes and organic substances upon the physical character of the clay suspensions.

The apparatus itself is exceedingly simple, the disc being suspended from a steel wire 11 ft. 6 in. long, and allowed to rotate within a vessel filled with the clay slip, figure 1. At the center of the brass disc filled with lead, a rod projects, provided with a clamp for gripping the wire firmly. An aluminum pointer is fastened to the rod which swings over a circular scale around the rim of the receptacle, graduated in degrees. This scale is made out of paper and varnished. The weight of the disc is 1333 grams and the thickness of the wire 0.85 mm.

In making the test the slip is first thoroughly stirred up and poured into the vessel. The disc is then turned about 180° by means of the pointer and released. The number of degrees is read off at the turning point of the vibration so that the amplitude of each swing in the same direction is observed. This is continued until several readings have been taken. The disc is then stopped and the slip stirred up for another set of check readings. The ratio of the amplitude of two successive swings is obtained by dividing the first reading into the second, the second into the third, and so on. This ratio is a constant for the same slip at the same temperature. It is important to make note of the temperature, or better to keep it constant, since the viscosity of the water itself changes with change in temperature.

The time of periodic vibration is obtained by taking the total of, say, ten complete vibrations and dividing by 20. It may also be calculated from the length of the wire. For the apparatus in question the periodic time of vibration was found to be 3.6 seconds, thus enabling two observers to make the readings quite readily.

Knowing the period of oscillation and the ratio of the amplitudes we can calculate the viscosity of water and that

of the slips to be compared with it. In this work the viscosity of water is always used as the standard, and hence the viscosities obtained are in terms of the viscosity of water.

Several methods of calculation might be employed, based upon the laws of the dampening of vibrations. Assuming for instance that the ratio of the amplitudes is 0.8 and the time is 1.5 seconds for each vibration, we obtain as an expression for the viscosity of the liquid:

$$0.8 = e^{-1.5k} \text{ or}$$
$$-\log 0.8 = 1.5k \log e.$$
$$\text{Then } K = \frac{-\log 0.8}{1.5 \log e} = 0.15$$

If in another slip the ratio of the amplitudes is found to be equal to 0.7 and solving again for K we obtain 0.24. The viscosities of the two liquids, therefore, are to each other in the ratio of 15 : 24. A somewhat simpler relation might be used for determining the relative though, of course, not the absolute viscosities, in which

v_1 = coefficient of viscosity of one liquid;

r_1 = ratio of the amplitudes of any two successive oscillations in the same direction in the same liquid;

T_1 = period of oscillation;

d_1 = dampening constant.

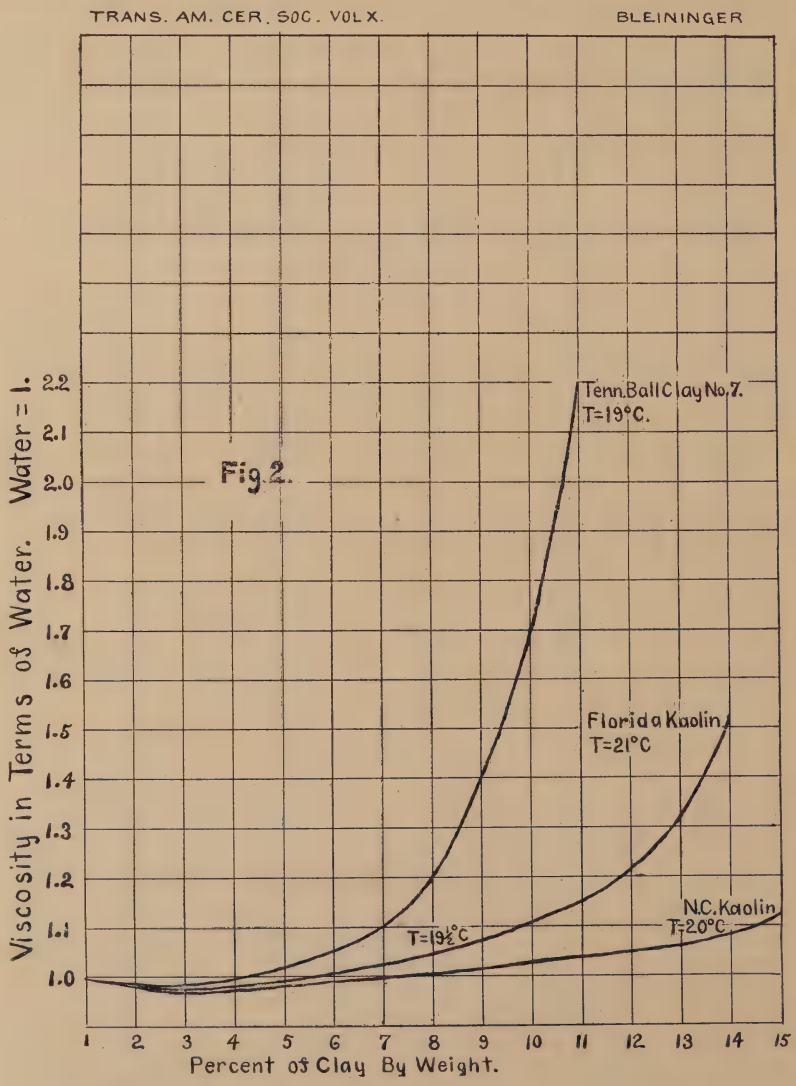
Similarly let v_2, r_2, T_2 and d_2 be the corresponding values for the second liquid. We have then the relation

$$\frac{d_1}{d_2} = \frac{T_2 \log r_1}{T_1 \log r_2} = \frac{v_1}{v_2} = K$$

This gives us K, a coefficient of specific viscosity. The standard employed is distilled water whose ratio is determined at the same temperature as the ratio of the slips to be tested. The constant for water, of course, differs with different apparatus. In the experiments carried on in the apparatus described it was 0.89.

It was decided to make viscosity determinations with three kaolins which differ widely in their physical behavior.

The method obviously is not intended for clays which are coarse-grained, and if they are to be tested in this way the coarser portion must be screened off. The three clays se-



lected were the North Carolina kaolin, Florida kaolin, and the Tennessee ball clay, No. 7.

The clays were weighed out, the moisture factor being allowed for, and mixed with a weighed amount of distilled water. The mixing was done in a small gallon porcelain ball mill, it being run for forty minutes in each case. The heaviest slip employed consisted of 85%, by weight, of water and 15% of clay, the apparatus not being able to vibrate in thicker slips. The 15% slip was at first blended with a 1% suspension for the intermediate compositions, but later the heavier slip was diluted with the distilled water alone. The blending was accomplished by simply stirring in a pitcher. In Fig. 2 will be found the viscosity curves of the three clays for different concentrations. They were the average of 30 determinations in each case, and the readings showed a variation of about ± 2%. It will be observed that at first the viscosity was decreased, a fact which is quite interesting. The Florida kaolin occupies a position midway between the North Carolina kaolin and the ball clay, but nearer to the kaolin than to the latter.

Might it not be possible that by this or other viscosity measurements we shall be enabled to correlate or classify our plastic clays? The practical potters constantly call our attention to the fact that we disregard the physical properties of kaolins, and that in our ceramic schools we do not properly discriminate in their use in our experiments. It is our duty therefore to employ such means as these to help them, as well as to push forward our knowledge of the elusive properties of clays.

As has been said, this apparatus is very delicate, and such things as the use of hydrant water in place of the distilled will cause marked changes in the behavior of the clays. This naturally leads to the action of salts like sodium carbonate, sodium silicate, etc., which opens up a large field of experimentation.

The work is to be continued with a modified apparatus which it is intended to operate in heavier slips.

A COMBINATION GAS AND STEAM POWER PLANT.

BY

GEORGE N. JEPPSON, Worcester, Mass.

At our fall meeting in 1906 we had the pleasure of listening to a lecture by Mr. S. S. Wyer on producer gas. The writer will endeavor to add a few notes as an appendix to the discussion which took place at that time.

Before referring to the gas plant proper, I wish to say a few words regarding the problem which confronted the Norton Company, Worcester, Mass., in the spring of 1906.

Our power plant at that time consisted of three Westinghouse compound non-condensing engines, two of them being 200 H. P. belt-driven and one 250 H. P. direct-connected to a 150 K. W. generator. Steam was generated in two vertical Manning tubular boilers and two Cahall water tube boilers. Our reason for running these engines non-condensing was because of our heating problem, a number of dry houses, as well as heating our plant in winter taking a large amount of steam, and it being our belief that as long as we were using all our exhaust for heating, that this plant was a very economical one.

We were, however, getting to the point where we could not use all the exhaust, and were also in need of more power in our works. After considering this watter very carefully, we decided to supplement the steam equipment with a bituminous producer gas plant and engine of 500 H. P., and to use the steam engines only to the point where all the exhaust could be taken care of for heating.

PLAN OF WORKS.

A plan of the works will show the location of the power house, it being about in the center of the plant. Steam for heating is circulated by a vacuum system and power is distributed by motors, large tools being direct driven and smaller ones by the group system.

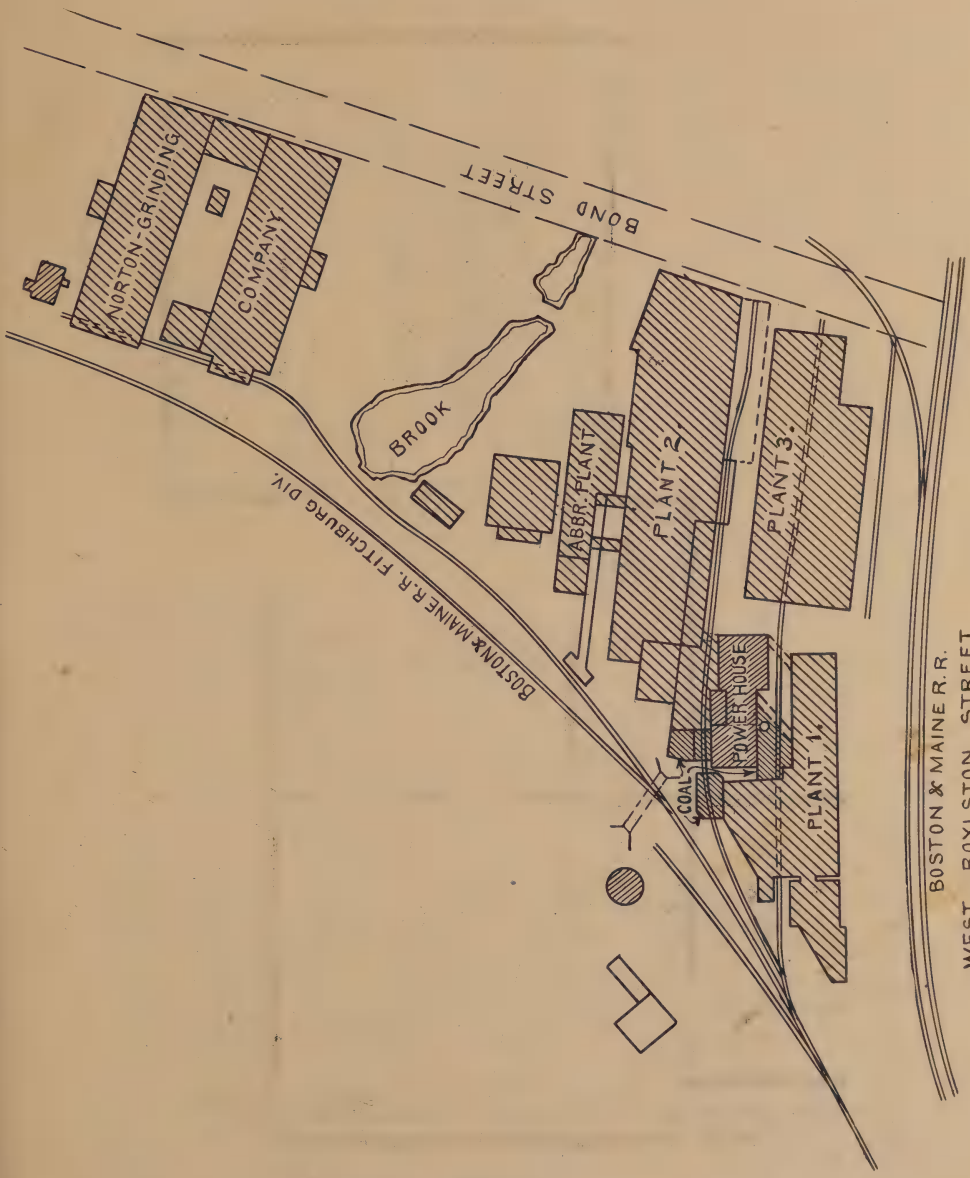

BOND STREET
NORTON-GRINDING COMPANY
BROOK
ABBR. PLANT
PLANT 2.
PLANT 3.
POWER HOUSE
PLANT 1.
COAL
BOSTON & MAINE R.R. FITCHBURG DIV.
BOSTON & MAINE R.R.
WEST BOYLSTON STREET

FIG. 1

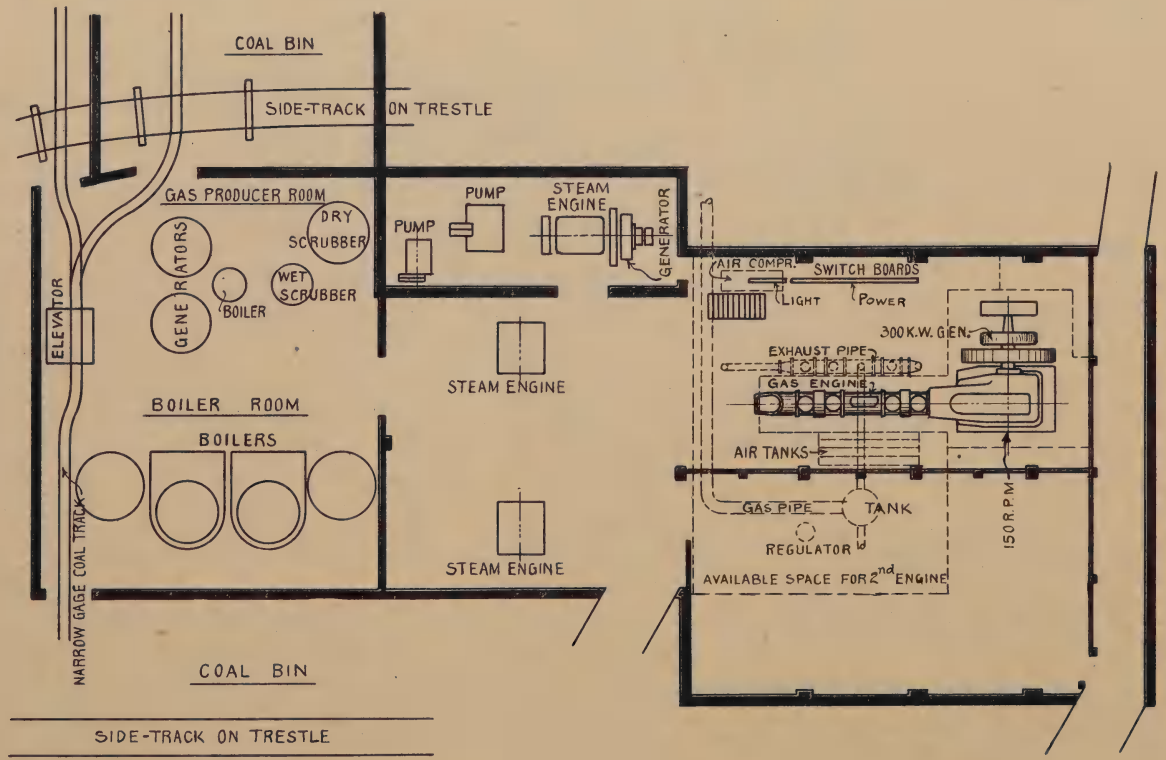

COAL BIN
SIDE-TRACK ON TRESTLE
GAS PRODUCER ROOM
DRY SCRUBBER
WET SCRUBBER
GENERATORS
BOILER
ELEVATOR
PUMP
PUMP
STEAM ENGINE
GENERATOR
AIR COMPR.
SWITCH BOARDS
LIGHT
POWER
300 K.W. GEN.
EXHAUST PIPE
GAS ENGINE
STEAM ENGINE
BOILER ROOM
BOILERS
AIR TANKS
GAS PIPE
TANK
REGULATOR
150 R.P.M.
STEAM ENGINE
AVAILABLE SPACE FOR 2nd ENGINE
NARROW GAGE COAL TRACK
COAL BIN
SIDE-TRACK ON TRESTLE

FIG. 2

PLAN OF POWER PLANT.

From the plan of power plant it will be noted that the boilers and gas producers are brought together for convenience in operating. Coal is stored on both sides of the building, the elevation of the railroad tracks allowing dumping directly into the bins, and from the bins the fuel is brought by a narrow gauge track into the power house and elevated to chutes for boilers and charging floor of producers by plunger elevator of two thousand pounds capacity, having a weighing scale incorporated in its platform.

In the engine room, space is provided for another gas engine of the same capacity as the present one, piping from the gas engine to holder being ample for 1000 B. H. P.

DESCRIPTION OF GAS PLANT.

The plant installed contains as its essential features a 500 B. H. P. Westinghouse horizontal four-cycle, double-acting engine with a 300 K. W. direct generator and a bituminous gas generating unit of the intermittent type, Loomis & Pettibone make, built by the Power & Mining Machinery Co. The producer plant consists of two 250 H. P. downdraft generators, a steam boiler, a Root blower, steam driven, and wet scrubber, dry scrubber and a holder of 15000 cu. ft. capacity, operated according to the following sketch.

The gas, as made, passes downward through an incandescent fuel bed. Any tars that are present are changed to fixed gases. From the producers the gas passes through the boiler, where the initial heat of the gas is used for generating steam. This steam is used for making water gas and for running the exhauster. Any surplus is used in the heating system. From the boiler, the gas passes through the wet scrubber to the dry scrubber and then to the holder, from whence it is fed to the engine at about four inches pressure.

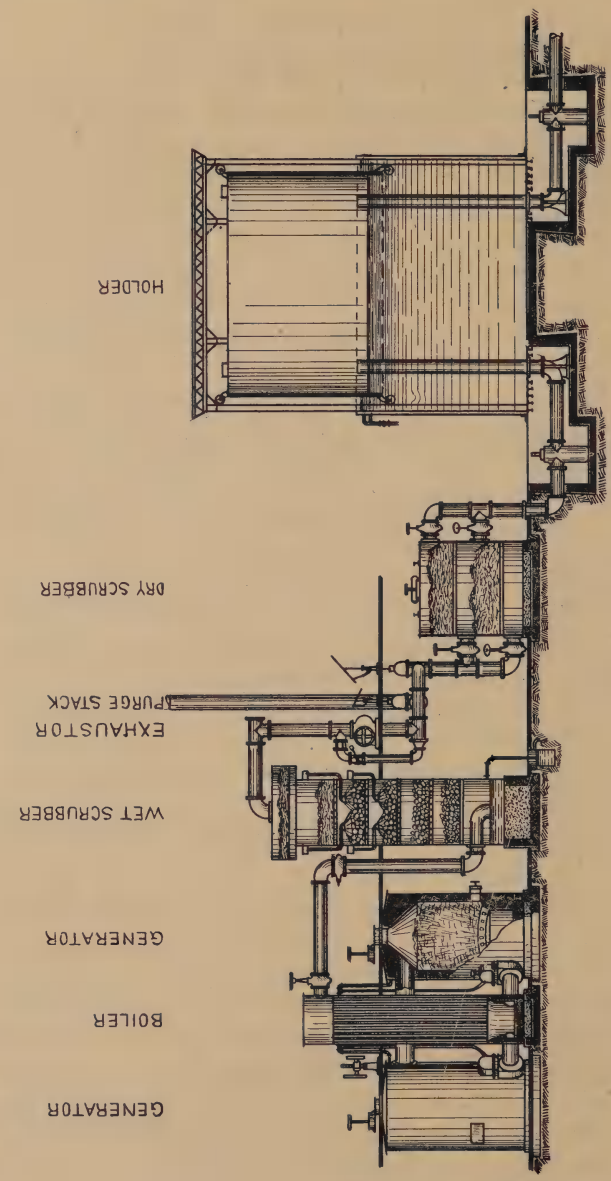

GAS GENERATING SYSTEM.
GENERATOR
BOILER
GENERATOR
WET SCRUBBER
EXHAUSTOR
PURGE STACK
DRY SCRUBBER
HOLDER

FIG. 3

FIRING OF PRODUCERS.

The producers, after cleaning, are first charged with coke, this fuel being the best and cheapest for getting the plant into operation in the shortest time for starting. It is our practice to put in a bed of coke about three feet thick, then wood on top of that. This is fired, and as soon as the coke ignites we immediately begin to build up the fires with coal.

During the day coal is fed as required, and water gas is made during half a minute every twenty to thirty minutes. This water gas is mixed with the producer gas in the holder. The making of water gas prevents the fires from getting too hot and the ash from clinkering. From the time fires are started, the engine can be running in forty minutes. Week days, when fires are banked over night, we are ready to start in twenty minutes from the time gas making begins, the holder being always left charged with gas when gas making is stopped.

The water consumption in the wet scrubber is 3000 gal. per hour or 6 gal. per B. H. P. This water, after performing its work, goes to waste. It is, however, passed through a settling tank which contains filters stuffed with excelsior, which collect the lampblack in suspension and leave the water clear. This lampblack is sold at 1½c per pound. We produce 200 lbs. per month.

FUEL.

Pocahontas steam coal, or a grade equal to it, we find to be the most economical to use. Coal that is high in ash or that clinkers causes more frequent cleaning, which is uneconomical on account of the labor required, fuel lost and also the wear and tear on the producer walls. With good coal, the longest period we have gone without cleaning is two weeks. With the average run, we clean once a week.

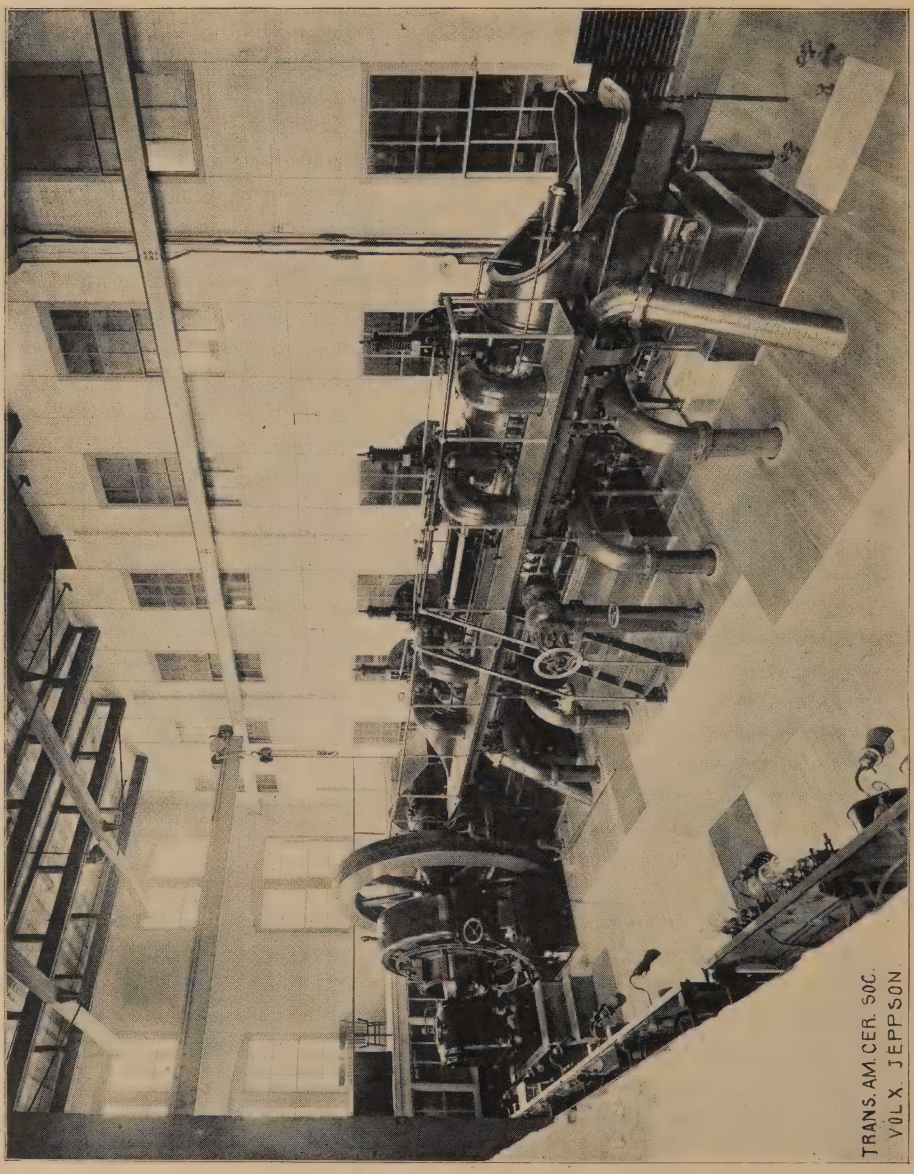


FIG. 4

AVERAGE ANALYSIS OF POCAHONTAS COAL.

Physical Water	.93
Volatile Combustible	11.21
Fixed Carbon	80.88
Ash	6.98
	100.00

AVERAGE ANALYSIS OF PRODUCER GAS.

Carbon Monoxide (CO)	3.9
Methane (CH_4)	23.8
Hydrogen (H_2)	1.1
Carbon Dioxide (CO_2)	8.8
Nitrogen (N_2)	62.4
	100.00

DESCRIPTION OF GAS ENGINE.

The general dimensions of the engine are 42′x17′. Its extreme height is 13′. It occupies about two square feet per K. W. This amply provides for all necessary passages and auxiliary apparatus. Stroke is 33½″, cylinder diameter 22½″ and speed 150 R. P. M. With generators, the weight is 101 tons. Ignition is by two independent systems, one of the familiar make and break, operated by a lay shaft paralleling the cylinders, the other a magnetic system, operated through the medium of electro magnets. Governor control is at the inlet valve, where the proportioning of gas and air and the mixing thereof is carried out. Starting is by compressed air at 240 lbs. pressure stored in tanks charged by electric driven compressor.

LUBRICATION.

The cylinders are lubricated by force feed oilers, and all journals and bearings by a gravity system. About three gallons of cylinder oil and about ten gallons of machine oil are used per week.

WATER COOLING.

Piston rods, cylinders and exhaust valves, those parts of the engine which are subject to the heat of combustion,

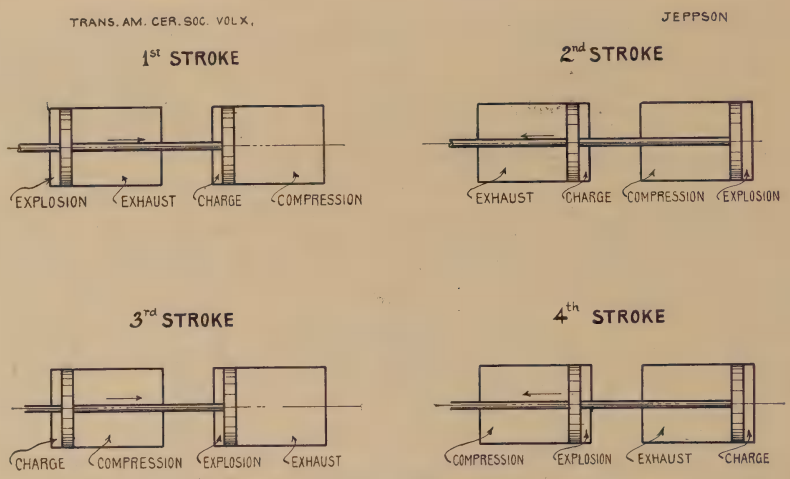

TRANS. AM. CER. SOC. VOL X.
JEPPSON
1st STROKE
EXPLOSION
EXHAUST
CHARGE
COMPRESSION
2nd STROKE
EXHAUST
CHARGE
COMPRESSION
EXPLOSION
3rd STROKE
CHARGE
COMPRESSION
EXPLOSION
EXHAUST
4th STROKE
COMPRESSION
EXPLOSION
EXHAUST
CHARGE

FIG. 5

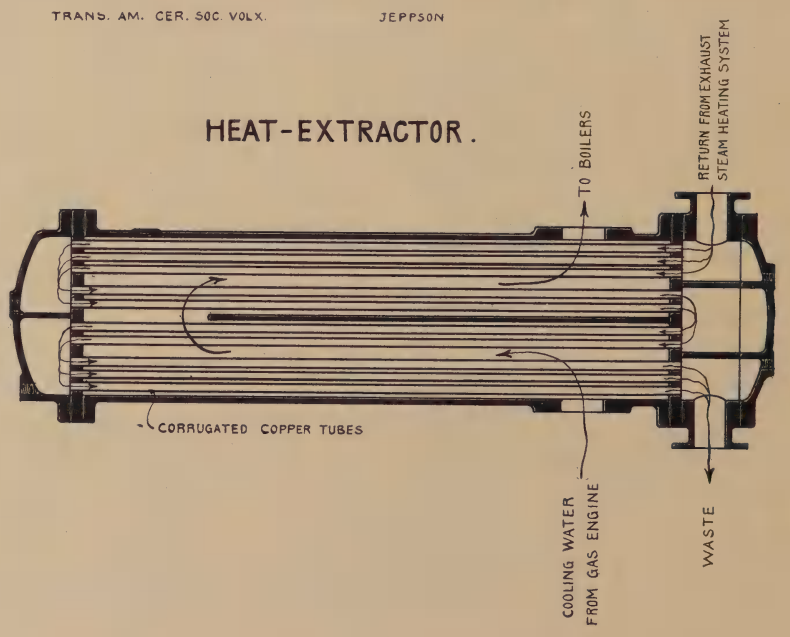

TRANS. AM. CER. SOC. VOL X.
JEPPSON
HEAT-EXTRACTOR.
TO BOILERS
RETURN FROM EXHAUST STEAM HEATING SYSTEM
CORRUGATED COPPER TUBES
COOLING WATER FROM GAS ENGINE
WASTE

FIG. 6

are water cooled. We use five gallons of water per B. H. P. per hour. This water is raised to about 110° F., and we find that if this type of engine is run hotter, we have trouble from pre-ignition, causing back-firing. This water is used in the boilers after first passing through a so-called "heat extractor," which is heated by the return water from the heating system. This apparatus raises the temperature to 175° F.

The use of this water by the method described is equal to a saving of 10.4% of the coal used for the steam plant. The return water from the heating system cannot be used for boiler feed on account of the oil which it contains, due to the steam engines.

The following chart represents the average coal per K. W. H. and per E. H. P. used by the gas plant per month, all standby losses being taken into account. It also shows the load curve in K. W. hours per month:

Power is measured by watt meter, readings being taken morning and evening and all coke and coal is weighed. The plant is run ten hours per day with half day on Saturday, giving a 36 hour shut down over Sunday.

It will be noted that June shows high in coal consumption, this being due to the tests made during this month by the Westinghouse Machine Company on the efficiency of the engine. In September we had an unusually poor run of coal. December shows high on account of the works running on short time and the engine running only to 70% of its rating, standby losses in the producer plant being necessarily the same as when running full load. Our average coal consumption for the entire year per E. H. P. was 1.6 lbs. per hour.

ATTENDANCE.

For the entire plant, we have one chief engineer, one gas engine attendant, one steam engine attendant, one gas maker, and two boiler firemen. It takes three men seven hours each at the weekly cleaning of producers. A gas fireman during the week could easily handle a 1000 H. P. producer plant.

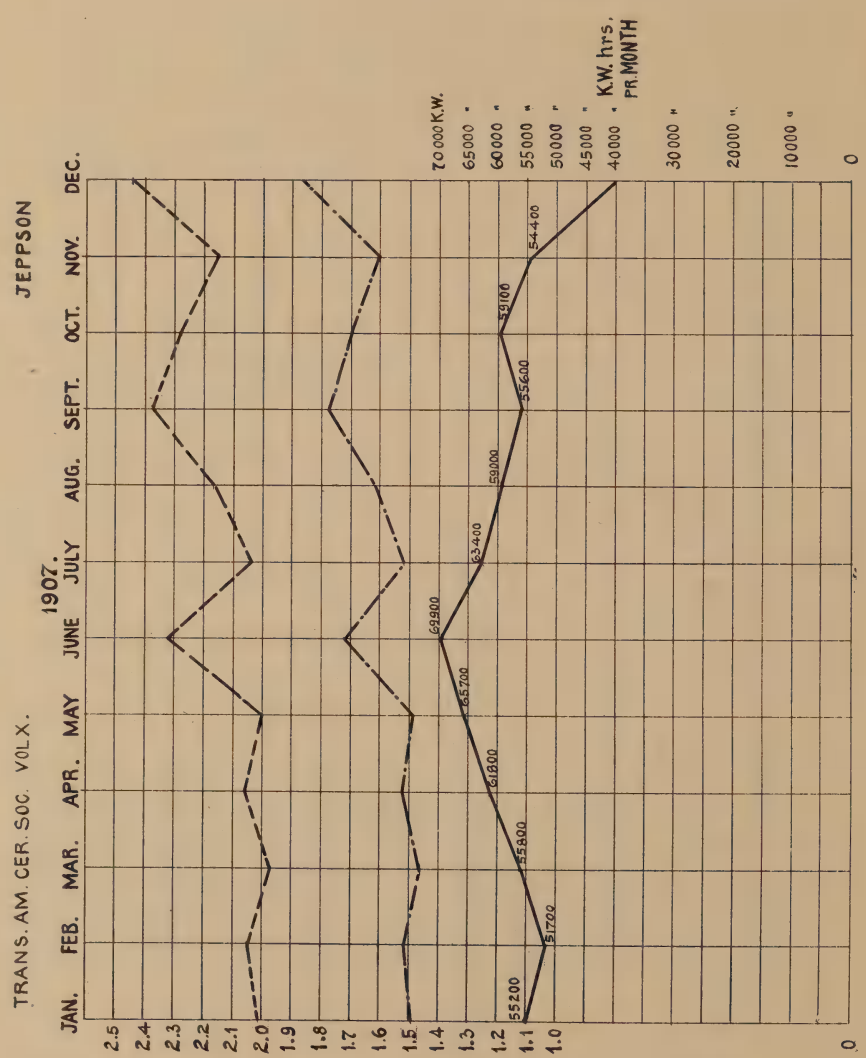

TRANS. AM. CER. SOC. VOL X.
JEPPSON
1907.
JAN. FEB. MAR. APR. MAY JUNE JULY AUG. SEPT. OCT. NOV. DEC.
LBS. COAL PR. K.W. hr.
LBS. COAL PR. EL. H.P. hr.
K.W. hrs. PR. MONTH
70000 K.W.
65000 "
60000 "
55000 "
50000 "
45000 "
40000 "
30000 "
20000 "
10000 "
0
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0
55200
51700
55800
61800
65700
69900
63400
59000
55600
53100
54400

FIG. 7

COST OF GAS PLANT.

The cost of this plant per B. P. H., including electric generator, producer plant, holder, piping and erection, was $84.43.

COST OF POWER.

Our figures show that we can produce a B. H. P. per year with the gas plant for $30.00. With the old steam plant, it cost us $45.00. This is for ten hours a day for approximately three hundred working days a year. These figures include coal, labor, supplies, interest on investment, and depreciation of plant.

GENERAL COMMENT.

The plant has given us no more trouble than a steam plant of the same size. Our log shows that from Jan. 1, 1907, to date, we have shut down only thirty-four minutes, this being due to ignition troubles once, poor gas once, and an obstructed cooling pipe once. The plant is not offensive to the neighborhood, and noise from the exhaust is no more than from a steam engine of the same capacity. The exhaust valves have been ground once since starting, and will probably run nine months without grinding. Inlet valves were examined after twelve months' run, and found in good condition and absolutely needed no grinding. A spare set of ignitors are carried and those in use are changed once a week. No trouble is occasioned in starting, it being posisble to be up to full speed in as short a time as one-half minute, the usual method of starting being to run on air for six or eight revolutions before turning on the gas.

In general, from our experience with this plant, we believe it to be both economical and dependable.

DISCUSSION.

Mr. Parker: Did I understand that the plant is run day and night? I would like to ask whether they bank the fires or not?

Mr. Griffin: The manufacturing departments run only ten hours a day. When the engine is shut down at night, the producers are left just as they are until it is time to start up the following morning, no coal whatever being used.

Mr. Parker: You are using live steam for heating?

Mr. Griffin: Live steam is used only when steam engines are shut down.

Mr. Parker: I will ask whether the economy from this system would apply to a brick plant where continued heating has to go on?

Mr. Griffin: From our experience, we believe that in any plant where the heating problem is a serious one, low pressure boilers for heating and gas engines for power, would be the most economical.

Mr. Parker: I believe the gas engine system of power is the coming system, but I do not exactly see how it can be applied to a plant which has to use a large amount of heat night and day. But if there is any way of getting heat from the exhaust gases, which I do not suppose is possible, it might prove economical.

Mr. Griffin: Using the heat from the exhaust of the engine has been attempted, but we have never heard of any success in this line.

Mr. Griffin: The water used in cooling the cylinders afterwards goes to the steam boilers. It leaves the engine about 110°F. This water passes through the heat extractor and is raised to 175° in temperature before going to the boilers.

Mr. Fisk: I would like to ask what is the comparative cost of the plant as described and a plant of similar capacity, complete, for operating by steam? I understand the cost of installation of this is eight-four dollars per H. P. Do you know how this compares?

Mr. Griffin: I have no figures on that.

Mr. Fisk: Can you give the cost of operating?

Mr. Griffin: With the plant as we had it before we put in this system, it cost us about forty-five dollars per

H. P. per year, but by this system this is brought down to thirty dollars.

Prof. Wheeler: If the gas holder is filled with gas, are you able to start with a full load?

Mr. Griffin: Yes. We could run on a full load for about fifteen minutes.

The Chair: This is a very fruitful discussion. Those who are acquainted with European conditions realize that the use of gas producer plants is far more extensive there than in the United States. The last time I was across I was surprised to observe the great development of the producer gas engine. Of course, there the fuel question is far more important, and they are compelled to look after the cost of power much more closely than we are. But I am convinced that in time the same conditions will arise in the United States; and it would be a good thing for those who are acquainted with the use of gas for power and other purposes to tell us something about their experience.

Mr. Plusch: As the question of fuel is one we are all interested in, I would suggest that those having questions to ask write them out and that the author of this paper be asked to answer them for publication in the report of this meeting.

Mr. Fisk: I think it would be interesting to have it stated in the report of this meeting whether $84.00 per H. P. included the cost of the building as well as the apparatus.

Mr. Griffin: It will be noted from the paper that the cost of plant covered generator, producer plant, holder, piping and the erection, but did not include the building.

Mr. Langenbeck: I was not present during the reading of the first part of the paper. Is this ordinary producer gas from coal or is it water gas produced from coke and steam, such as is used in German plants?

Mr. Griffin: It is part water gas and part coal gas.

Mr. Langenbeck: Almost entirely water gas?

Mr. Griffin: *No.*

Mr. Langenbeck: Is it something between the ordinary producer gas and the ordinary air-water gas?

Mr. Griffin: In our plant we have a steam boiler in which the steam is generated by the initial heat of these gases. In order to keep our fires clean, every half hour we blow a jet of steam up through one and down through the other producer. It cleans the fires and loosens the clinkers and gives a run of two minutes out of a half hour on straight water gas. We do not like to run longer, because we believe the troubles from back firing are caused by too much hydrogen. We do make a little water gas which is mixed with the producer gas.

Mr. Langenbeck: Has any analysis been made of that gas? I ask that question because the paper is altogether in the light of power production; but it naturally occurs to a ceramist to what extent such gas could be used as a source of heat for kiln firing of some kind. Will it run too high in nitrogen?

Mr. Griffin: It will run about 62% nitrogen. I have the analysis here with the paper.

Mr. Cannon: The question has come up about drying and heating with producer gas. It is claimed, I believe, that you can even use the gas from the engine in radiators around a plant. In our clay working plants we use a little more steam for drying and heating for seven months of the year than it takes for power. It is claimed that a radiating system is being developed now to pipe this heat of the exhaust gas to any part of the plant and use it. It would have to be a fireproof building, of course, in which it could be used. As to the cost, I heard it estimated by a representative of a firm that wanted $90.00 per H. P. Mr. Griffin said it cost $84.00. The engineering companies will quote about $60.00 per H. P. for equipment, without building, for steam.

Mr. Fisk: For steam?

Mr. Cannon: Comparing the cost of steam to that of the gas apparatus, one is about ninety and the other sixty. It is about twenty per cent less for a steam plant.

but they claim forty percent instead of thirty percent, as here given, as saving in cost of operation.

Mr. Wheeler: I desire to ask the following questions to be answered by the author of the paper and incorporated in the published report:

What cost for coal per ton is the H. P. figured on?

What rate is depreciation figured at in the cost sheet?

Is the tar recovery of value as a by-product?

The Author: The H. P. is figured with coal (Pocahontas) at $5.00 per ton.

The rate of depreciation is figured on the cost sheet at 3%.

By the Loomis-Pettibone system, there are no tars. As the gases pass downward through the generator, they are changed into fixed gases, so that no traces of tar are ever seen in the piping. We do, however, recover as a by-product some lampblack from the wet scrubber, for which there is a market.

A STUDY OF THE HEAT DISTRIBUTION IN FOUR INDUSTRIAL KILNS.

BY

A. V. BLEININGER, Champaign, Illinois.

There is a decided lack of data in regard to the consumption of fuel in periodic ceramic kilns, expressed in accurate terms, as well as with respect to the way in which the heat is distributed. It was hence thought advisable to undertake the examination of several kilns for the purpose of determining the ratio between the heat made useful and that escaping as waste. The kilns studied represented several types and widely differing conditions, one of them being a sewer pipe, one a paving brick, and two, terra cotta muffle kilns, entirely unlike in construction. In addition a building brick kiln was examined, which has already been reported upon elsewhere.*

In making a heat balance of a kilns we must determine the following factors:

A. Heat introduced as fuel.
B. Heat lost by the waste gases.
C. Heat lost by the unburnt fuel in the ashes.
D. Heat used in the burning of the ware.
E. Heat taken up by the kiln and lost by radiation.

The last factor, important though it is, cannot be estimated by any direct means available, since the difficulties opposed to its determination are too great. We must be satisfied to obtain it by difference. For, since the first four items are readily obtainable by measurement, the fifth is arrived at by the evident relation:

$$E=A-(B+C+D).$$

*"The Balance Sheet of a Down Draft Kiln," *Clay Worker*, February, 1908. Read before the N. B. M. A.

A. The heat introduced as fuel was of course readily calculated from the weight of the coal used from day to day. The calorific value of the latter was obtained by determining the heating value of a well averaged sample of the fuel in the calorimeter. This work was done in the department of industrial chemistry at the University of Illinois, under the direction of Professor Parr. The weight of the coal multiplied by its heating value gave the total number of calories introduced.

B. The heat carried out by the waste gases was calculated from the daily coal consumption, the ultimate analysis of the coal, the analysis of the stack gases, the thermal capacity of the gases and the flue temperature. The first factor was, of course, easily determined by weighing the coal, the second by the ultimate analysis of the coal, this work having been carried out in the department of chemistry under Professor Parr, the third by the analysis of the flue gases, using the Orsat apparatus, the fourth from known data, and the fifth by means of the Le Chatelier thermocouple applied in the flue as close to the kiln as possible.

The daily coal consumption permitted of calculating the weight of coal fired per hour for a certain period, which was, for the sake of convenience, taken as twelve hours. This period was considered the unit in all the calculations.

From the ultimate analysis, allowing for the carbon escaping with the ashes, the weight of the gases evolved with theoretical air supply was calculated. If, for instance, the coal had the following composition:

Carbon	60.15%	—3.03 (lost in ashes)	=57.12%
Hydrogen	4.15%		
Oxygen	9.37%		
Sulphur	4.34%	—1.30 (lost in ashes)	= 3.04%
Moisture	7.90%		
Ash	14.09%		

1 kg. of coal would result, on burning with just the requisite amount of air, in

$$0.5712 \times \tfrac{44}{12} = 2.09 \text{ kg. of carbon dioxide}$$
$$0.0415\ 9 + 0.079 = 0.453 \text{ kg. of steam}$$
$$0.0304 \times 2 = 0.060 \text{ kg. of sulphur oxide}$$
$$0.5712 \times \tfrac{32}{12} \times 3.35 = 5.900 \text{ kg. of nitrogen}$$

The weight of air required for the combustion of 1 kg. of this coal would then be 7.66 kg.

The flue gas analysis was simply made for the purpose of determining the amount of excess air introduced into the kiln, as this evidently changes the weight of the gases resulting from 1 kg. of the coal materially. It was endeavored to take samples from the flue so that they represented average conditions, and from two to three analyses were made each hour. This meant the making of hundreds of analyses during each burn. As the basis of the calculation of the excess air present the oxygen found was used according to the relation:

$$\text{Coefficient of air-admission} = \frac{100}{100 - 4.76 \times \%\ \text{Oxygen.}}$$

To illustrate: Supposing the gas was found to contain 5% of oxygen. We would have then:

$$\frac{100}{100 - 4.76 \times 5} = 1.31, \text{ representing total air admitted.}$$

The excess air must then be 1.31—1=0.31.

Applying this to the weights of the gases obtained above we would have:

2.090 kg. CO_2
0.453 kg. H_2O
0.060 kg. SO_2
5.900 kg. N_2
$7.66 . 0.31 = 2.370$ kg. Air

It might be added that the gas samples were taken as close to the kiln as possible, so as to avoid the dilution caused by the leakage of air into the flue near the damper.

In calculating the heat lost by the waste gases during any given period we must first obtain the ratio of the heat

carried out by the gases evolved from 1 kg. of coal at the flue temperature to the heating value of this weight of coal.

In this calculation there are necessary the weight of waste gases, their thermal capacity and the flue temperature.

The specific heats of the gases, as taken from the standard tables are not suitable for these calculations, since they apply only to a temperature range between 0° and 100°C, and if used would cause a more or less grave error. The work of Le Chatelier and Mallard* has clearly shown that the thermal capacity of gases is expressed by a parabolic formula of two parameters:

$$Qu = a\frac{T}{100} + b\frac{T^2}{1000^2}$$

in which Qu=heat capacity.
a=a constant comon to all gases=6.5.
T=absolute temperature.
b=a constant, variable for different gases.

The value of b for perfect gases like O_2, N_2, H_2 and CO is 0.6, for H_2O 2.9, and for CO_2 3.7. This formula applies only to the molecular volume of each gas at absolute temperatures. For the sake of convenience it is preferable to calculate the values in terms of one kg. and the temperature in degrees C. This has been done in the following table:†

THERMAL CAPACITY OF 1 KG. GAS, IN KG. CALS.

Temperature in degrees C.	Oxygen	Nitrogen, Carbon Monoxide	Steam	Carbon Dioxide
0	0.0	0.0	0.0	0.0
200	47.3	50.0	100.0	43.1
400	88.0	100.0	203.0	91.0
600	134.0	154.0	326.0	145.0
800	181.0	207.0	461.0	208.0
1000	232.0	264.0	609.0	277.0
1200	284.0	325.0	770.0	354.0
1400	334.0	383.0	943.0	435.0

*Industrial Furnaces and Methods of Control. Emilio Damour, p. 11. Metallurgical Calculations. J. W. Richards.

†Industrial Furnaces and Methods of Control. Emilio Damour, p. 13.

By plotting a curve from these data for each gas the heat capacity of 1 kg. of the gas can be read off at once for any temperature. This was done in the work under discussion. For the purpose of illustration let us take the figures obtained above for the weights of the gases, and assuming that the gases left the kiln ot 620°C we would have the following heat capacities, the atmospheric temperature being 20°.

$$\begin{aligned}
2.09 \times 145 &= 303.05 \text{ kg. cals., heat capacity of } CO_2 \\
0.453 \times 326 &= 147.68 \text{ kg. cals., heat capacity of } H_2O \\
0.453 \times 80 + 0.453 \times 537 &= 279.50 \text{ kg. cals., heat of vaporization of } H_2O \\
5.9 \times 154 &= 908.00 \text{ kg. cals., heat capacity of } N_2 \\
2.37 \times 149.4 &= 354.08 \text{ kg. cals., heat capacity of air} \\
\hline
&= 1992.31 \text{ total heat carried out by waste gases.}
\end{aligned}$$

If the calorific power of the coal used is 6200, it is evident that the heat lost by the waste gases must be equal to $\frac{1992}{6200} \times 100 = 32.13$ per cent. For every 100 pounds of coal fired we thus lose in the waste gases 32.13 pounds.

The temperature, as has already been stated, was obtained by means of the Le Chatelier thermocouple, inserted into the flue close to the kiln. Corrections were made for the atmospheric temperature. This was done by fastening a thermometer to the junction between the platinum and the copper wire. The correction is equal to 0.5 of the thermometer reading where the atmospheric temperature does not exceed 40°. In very hot places the correct procedure is to insert the copper junction in boiling water and to calibrate the couple under these conditions. The calibration is to be made by means of the melting points of zinc, silver and gold or copper.

In the losses due to the waste gases must be included also the loss due to the escape of combustible gases. Under the conditions of the kilns examined in this work the amount of carbon monoxide found in the gases was very small. Immediately after firing some of this gas was found, but it disappeared in a few minutes. For this rea-

son it was not included in the losses incurred by the flue gases. It seems that the hot mass of clay tends to promote the oxidation of the combustible gases formed in the furnace.

D. The heat required to raise the ware to the ultimate temperature of the kiln was calculated from the weight of the ware, its specific heat and the kiln temperature. The amount of water contained in the clay was taken into consideration. Unfortunately, several important constants are lacking, such as the heat of dehydration of clay and the heat of vaporization of the hygroscopic water. Even the specific heat of clay is not known for the higher temperatures, though it is usually given in text books as being 0.2. Mr. J. K. Moore, during some recent work in connection with his thesis, found the average thermal capacity of a burnt No. 2 fire clay between the limits of 400-1100°C to be 0.235. At the time the calculations for this work were made the specific heat of clay was taken as 0.2. The heat of dehydration was assumed to be 200 gr. calories per gram of water. No reliable data was obtainable on this subject. The latent heat of the hygroscopic water which leaves in the neighborhood of 200° was taken to be 476 according to the formula of Griffith's,

$$L=596.73-0.60t.$$

Assuming then a clay, containing 2% of hygroscopic and 7% of chemical water which is to be raised to 1120°, we would have for 1 kg. of the dried clay the following heat consumption, the atmospheric temperature being 20°. The dehydration temperature to be taken as 650°.

Hygroscopic water	$0.02\times180\times1=$	3.6 kg. calories
	$0.02\times476=$	9.5 kg. calories
Chemical water	$0.07\times.02\times650=$	9.1 kg. calories
	$0.07\times200=$	14.0 kg. calories
Clay	$0.93\times0.2\times1100=$	204.6 kg. calories
1 kg. clay thus requires		240.8 kg. calories

E. As has been mentioned above, the heat absorbed by the kiln and lost by radiation was obtained by difference.

APPARATUS.

The apparatus used in this work consisted of the Orsat gas apparatus, two tin gas samplers, supported by tripods and painted with asphaltum paint, one Siemens-Halske milli-voltmeter and double throw switch, two thermocouples, one for the flue, the other for the kiln, two thermometers reading to 100°C and two to 300°, the latter being used during the watersmoking period, and two Richardson-Lovejoy metal draft gauges, filled with colored petroleum and showing a reading magnified four times.

The gas was drawn from the flue through ¾″ pipes plugged at the end and perforated around the side. The pipe connected to the draft gauge was provided with an elbow so that the end of the pipe was parallel to the axis of the flue and pointed in the direction of the stack. This was found to be important, giving more consistent readings than when the pipe was inserted at right angles to the flue.

DRAFT GAUGE.

The readings of the draft gauge were not necessary for the determination of the heat escaping through the stack, since the weight of coal actually fired was used as the basis of the calculations, but they were useful in indicating the increasing velocity of the gases in the stack. The draft gauge without a Pitot tube cannot be used to measure the velocity of the gases except it is calibrated against an anemometer. A Pitot tube suitable for the purpose was not available, since the usual metal instrument would soon be destroyed by the high temperature of the gases and the time was too short for making a clay tube of this kind.

With the Pitot tube the velocity of the gases in the flue or stack is calculated from the relation.

$$V = \sqrt{2\ gh\ \frac{d_1}{d_2}}$$

where v=the velocity in feet or meters per second.

g=the gravity constant, 32.14 ft. or 9.8 meters.

h=*real* height of the petroleum column in feet or meters, shown by the draft gauge.

d=density of petroleum, in terms of water at 4°C.

d=density of the gases at the temperature and pressure of the stack or flue in terms of water at 4°.

The relation between the real velocity as determined by the anemometer and that calculated from the Pitot tube is approximately 1.1—1.2, for the velocities in question in ceramic stacks. The Pitot tube velocities are hence to be multiplied by this factor in order to obtain the real velocity.*

Some erroneous conceptions are current in regard to the meaning of the draft gauge readings. The value indicated by the gauge does not represent the total magnitude or "head" of the draft, but only that part of it which corresponds to the velocity of the gases and which is not available for pulling the gases through the furnaces and kiln.

The total head of draft which may be expressed in inches or millimeters of water or air at 0° is the pull obtained by a stack, measured by the difference in the weight of the hot gases occupying the chimney and the weight of the same volume of air at atmospheric temperature. To illustrate, assuming a stack 10 meters high and 1 square meter in cross section at 273°C, with the atmospheric air at 0°, we have a difference in weight as follows: The weight of 10 cubic meters of air (volume of stack) at 0°C= 12.93 kg. The weight of the same volume of air at 273°= 6.465 kg. We have, then, as the measure of the total draft the weight of 12.93−6.465=6.465 kg. This weight is distributed over the cross section of 1 sq. meter=10000 sq. cm. The pressure upon 1 sq. cm. is thus 0.65 gram. This corresponds to a height of a water column of 0.65 cm. Expressed in terms of air at 0° it is 0.65×772=501.8 cm., water being 772 times as heavy as air at the same tempera-

*W. D. Harkins and R. E. Swain. Jour. Am. Chem. Soc., Vol. 29, p. 970.

ture. This head of 5.02 meters represents the total draft. But only part of it is available for forcing the air needed for combustion into the furnaces and pulling out of the kiln the gases produced. Part of this force is taken up by the velocity of the stack gases and part of it by the friction of the gases in the stack. The head available for the kiln, then, is equal to the total head minus the velocity and friction heads.

The velocity head is calculated from the relation

$$h_1 = \frac{V^2}{2g}.$$

Assuming the velocity of the gases in the above stack to be 6 meters per second, the velocity head, h_1, becomes

$$h_1 = \frac{36}{2 \times 9.8} = 1.84 \text{ m., in terms of air at } 273°.$$

Reduced to terms of air at 0° this head becomes 0.92m. According to Richards the friction head, h_2, of a stack is:

$$h_2 = 1.9 - K\frac{H}{d}$$

where H=height of stack.
d=diameter or side of chimney.
k=constant, whose average value=0.08.

Substituting, we obtain

$$h_2 = 1.9 - .0.08\frac{10}{1} = 0.15 \text{ meters.}$$

The head of the stack thus available for pulling the gases through the kiln=5.02−(1.84+0.15)=3.03 meters of air at 0°.

Experimentally, the total head of a stack may be determined by suddenly dropping the damper and observing the draft gauge reading instantly. The common idea that the draft of a kiln is increased greatly as the stack becomes very hot is not true. It is true that the draft in-

creases up to a certain temperature but not beyond it, in spite of the fact that the velocity of the gases increases. But as we have seen, increased stack velocity means increased loss in available head. It must be remembered that the draft of a stack is not measured by the volume of the gases drawn off, but by the *weight* of gas removed per unit time.

We have thus the expression:

$$Qu = \frac{Sd\sqrt{2g\,0.00366.L\,(t_1 - t_2)}}{1 + 0.00366\,t_1} \quad \text{where}$$

Qu=the weight of the gases removed per second.
S =cross section of stack.
d =density of the gases at 0°.
g =9.8 m. or 32.14 feet.
L =height of stack.
t_1 =mean temperature of the gases in the stack in degrees C.
t =temperature of the air in degrees C.

Since here $Sd\sqrt{2\,g\,0.00366\,L}$=constant we may say that

$$Qu = K\frac{\sqrt{t_1 - t}}{1 + 0.00366\,t_1}$$

By differentiation or graphical determination of the maximum value of Qu we find that the temperature at which the greatest weight of gases is removed is at 273°C. Nothing is gained, therefore, as far as the *available* draft of a stack is concerned, by maintaining a mean stack temperature higher than 273° above the atmospheric temperature.

SEWER PIPE KILN.

The kiln in question was one of the older kilns on the plant and was rectangular, its dimensions being: Length, 42 feet, width, 17½ feet, height, 19 feet, inside measurements. It was set with double strength 20 inch pipe, nested with smaller sizes, and contained 120,460 pounds of clay, all told, including rings, etc.

In burning, 87,335 pounds of coal were used, which had the following composition:

Carbon	59.76%
Hydrogen	4.08%
Oxygen and Nitrogen	10.72%
Sulphur	2.57%
Ash	11.74%
Moisture	11.13%

The ash was found to show the following analysis:

Carbon	29.17%
Hydrogen	0.26%
Oxygen and Nitrogen	3.13%
Sulphur	3.16%
Ash	68.99%
Moisture	1.55%

The calorific power of the coal was 6,020 calories, or 10,837 B. T. U.

The weights of the gases from 1 kg. of coal were:

CO_2=2.070 kg.
H_2O=0.478 kg.
N_2=5.765 kg.

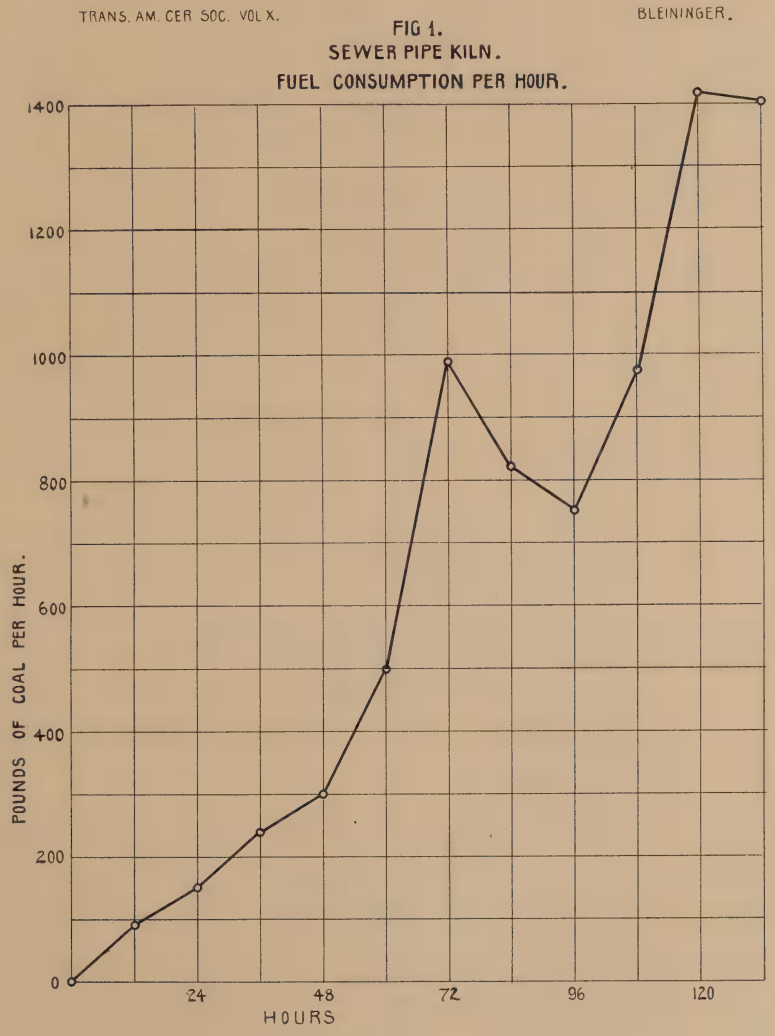
assuming perfect combustion. The weight of air required per kg. of coal is 7.48 kg.; 3.42 per cent of carbon were lost in the ashes.

The length of the burn was 129 hours. This was divided into 10 periods of 12 hours and one of 9 hours. All the analyses and other data were averaged on the basis of the 12 hour period, care having been taken to make the analyses representative of the average conditions.

In Fig. 1 we have represented the average coal consumption per hour during the burn. Fig. 2 shows the time-temperature curves of the kiln and flue. In Fig. 3 there are shown the average carbon dioxide and air percentages for each period throughout the burn.

HEAT LOST BY WASTE GASES.

In calculating the heat passing off with the waste gases from the data represented by the above curves, the *mean* flue temperature from the beginning to the end of each period was taken and the atmospheric temperature

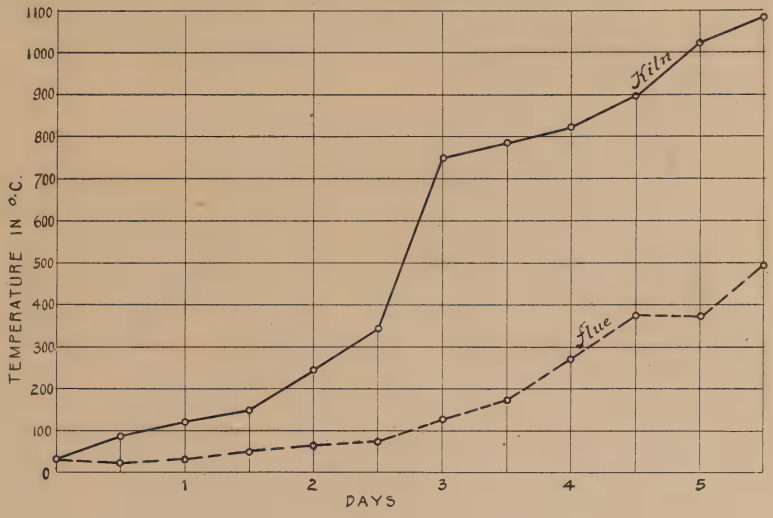


deducted. The heat carried out by the gases corresponding to 1 kg. of coal was then calculated, as shown in the first part of this paper. In the case of the sewer-pipe kiln the waste heat of each period is given in the following table:

Period	1	2	3	4	5	6	7	8	9	10	11
Kg. calories lost per kg. of coal	312	373	711	611	539	522	673	1250	1610	1450	1726
% lost in terms of heating value of coal	5.18	6.20	11.81	10.15	8.96	8.67	11.18	20.78	26.74	24.09	2867
Pounds of coal lost by waste gases per period	52.2	111.2	331	364	542	1030	1141	1886	3148	4131	3615

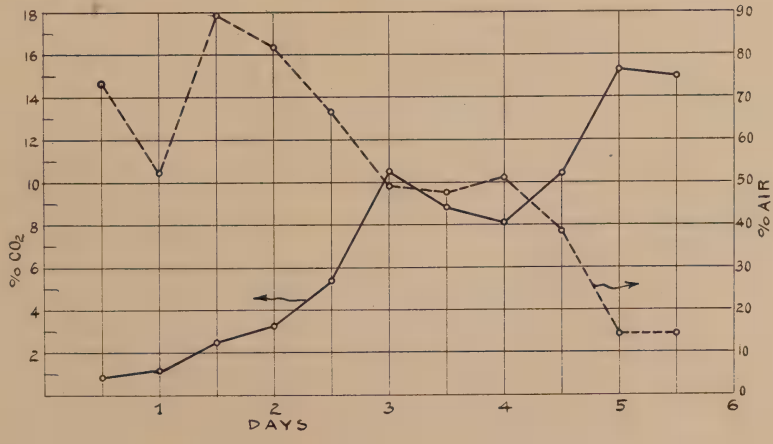
TRANS. AM. CER. SOC. VOL X BLEININGER

FIG 2.
SEWER PIPE KILN.
TIME - TEMPERATURE CURVE.



TRANS. AM. CER SOC. VOL X. BLEININGER

FIG3.
SEWER PIPE KILN.
AVERAGE CARBON DIOXIDE
&
AIR CONTENT OF FIRE GASES.



Adding up the pounds of coal which express the loss of heat by the waste gases we obtain 16351 pounds. Since the total coal fired was 87,330 pounds, it is evident that the heat escaping through the flue is equal to 18.6 per cent. Fig. 4 shows the losses for each period of the burn.

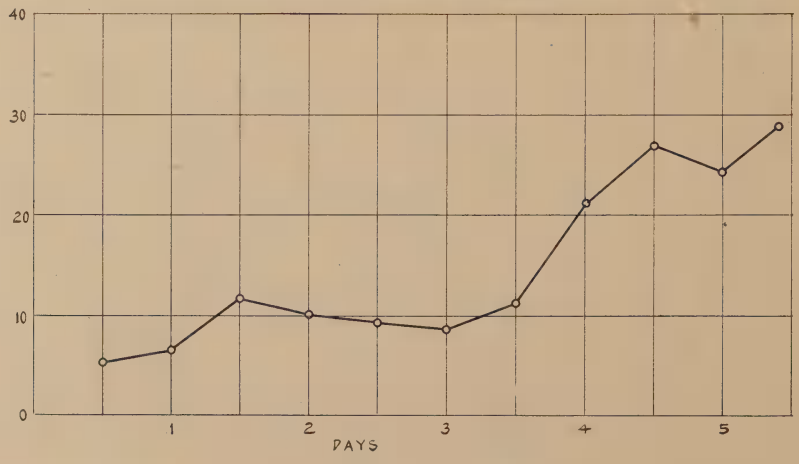
HEAT REQUIRED TO BURN THE WARE.

Calculating the heat required to burn 120,460 pounds of clay, as illustrated above, to a temperature of 1100° there will be used 13,689,179 kg. calories, which equal 4987 pounds of the coal employed in this case. This corresponds to 5.71% of the total heat introduced into the kiln.

HEAT LOST IN THE ASHES.

The carbon lost in the ashes amounts to 3.42% of the coal. Since practically no available hydrogen was found

FIG 4.
SEWER PIPE KILN.
%HEAT LOST BY WASTE
GASES IN TERMS OF HEAT INTRODUCED.



in the ashes, the heat lost in this way evidently is 0.0342× 8080 kg. calories per kg. of coal. Calculating this loss in percentage we obtain 4.58%.

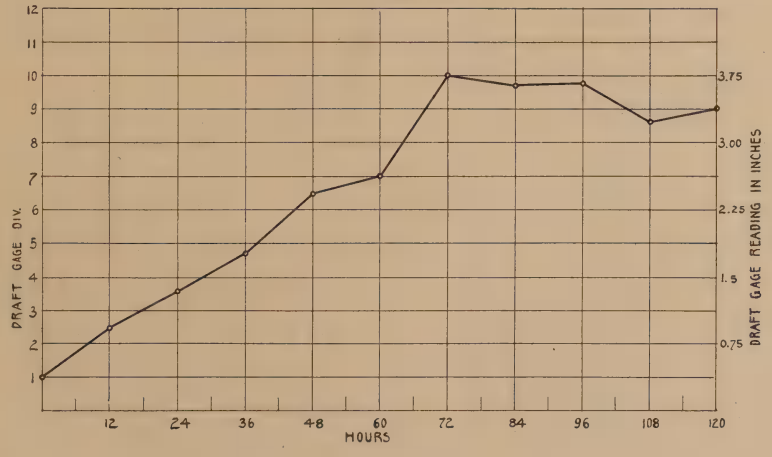
HEAT TAKEN UP BY THE KILN AND LOST BY RADIATION.

The heat coming under this heading is evidently obtained by subtracting the sum of 18.6%+5.71%+4.58% from 100 which gives us 71.1%, a very high percentage, approaching the similar losses of open-hearth steel furnaces and must be ascribed to the poor condition of the kiln.

In Fig. 5 the draft-gauge readings are plotted, expressed in draft gauge divisions and inches. The gauge was frequently set to the zero point to allow for the evaporation of the petroleum.

TRANS. AM. CER. SOC. VOL X. BLEININGER.

FIG 5.
SEWER PIPE KILN.
DRAFT GAGE CURVE.



Collecting the data obtained in these calculations we find the heat distribution to be as follows:

Heat lost by the fire gases	18.6 %
Heat taken up by the ware	5.7 %
Heat lost by ashes	4.58%
Heat taken by kiln and lost by radiation	71.1 %
	100.0%

In burning 1000 kg. of ware there were used 4378341 kg. cals.
In burning 1 ton of ware there were used 3984200 kg. cals.
In burning 1 ton of ware there were used 1456.8 lbs. of coal
Temperature 1100°C.

During salting the fire gases were found to contain 15.6% CO_2 and 2.4% O_2. An interesting fact observed was also that the temperature during salting rose 5° in spite of the fact that the reactions involved in salting are endothermic, thus showing that there is no difficulty in maintaining sufficient heat.

During the latter part of the burn some carbon monoxide was found in the gases, but only for a short time and in small amounts. The loss of heat due to this source was hence neglected.

PAVING BRICK KILN.

This kiln was a 26 ft. round down draft kiln and contained 357,264 pounds of burnt clay. The amount of coal used was 121,928 pounds. The maximum temperature reached was 1110°C.

Analysis of coal:

Carbon	60.15%
Hydrogen	4.15%
Sulphur	4.34%
Oxygen and Nitrogen	9.37%
Ash	14.09%
Moisture	7.90%

The calorific power was found to be 6231 or 11216 B. T. U.

Analysis of ashes:

Carbon	21.53%
Hydrogen	0.11%
Sulphur	1.81%
Oxygen and Nitrogen	0.83%
Ash	77.30%
Moisture	0.08%

Thus 3.03% of carbon in the coal was lost with the ashes.

From 1 kg. of this coal there would be evolved:

2.090 kg. carbon dioxide
0.453 kg. steam
5.900 kg. nitrogen

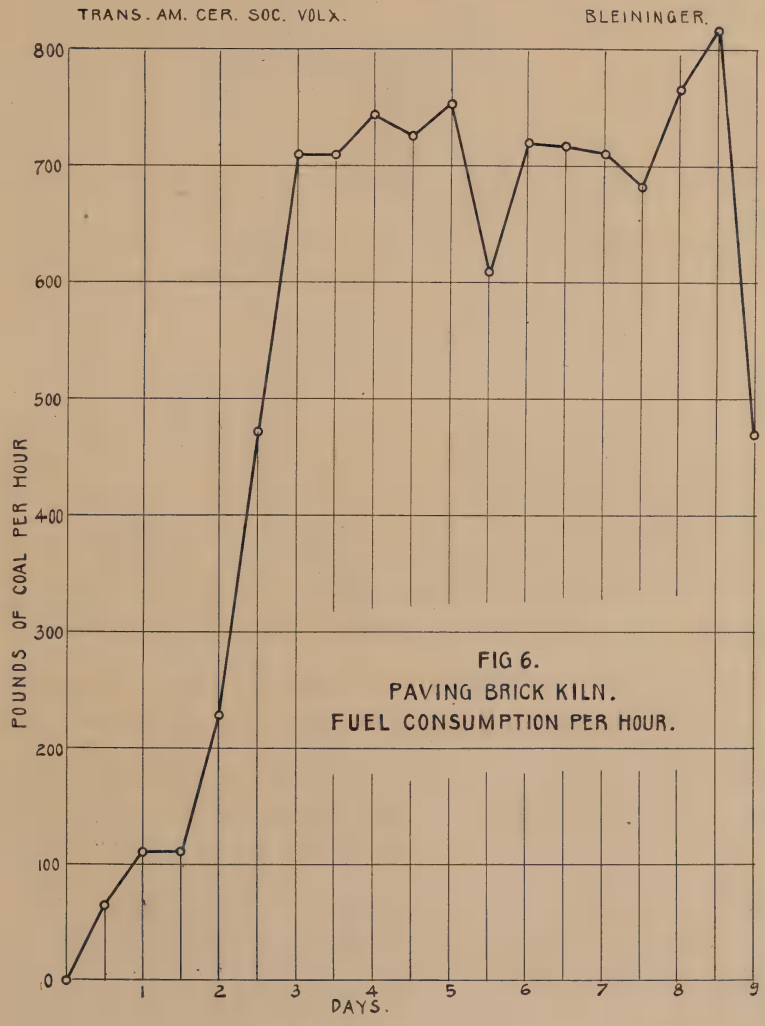
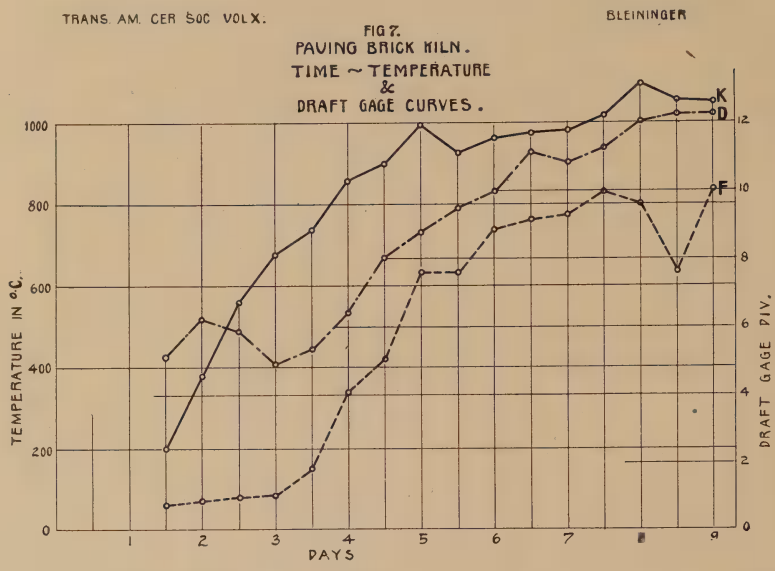


FIG 6.
PAVING BRICK KILN.
FUEL CONSUMPTION PER HOUR.

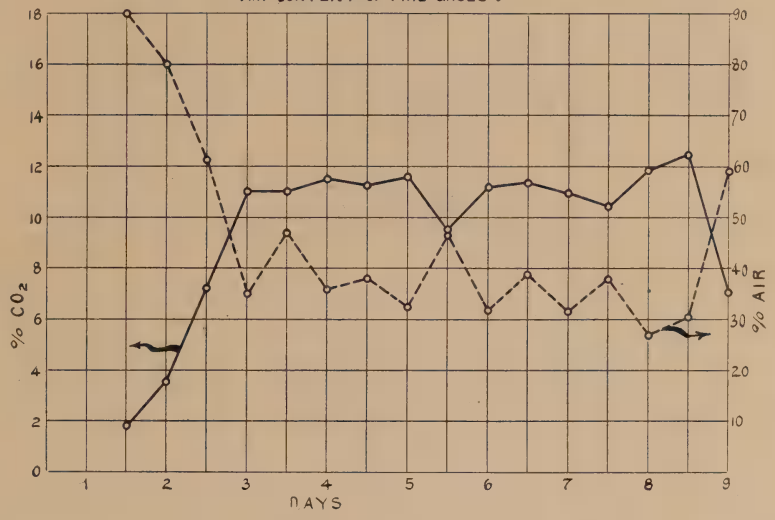


not considering the sulphur dioxide and assuming perfect conditions of combustion. For each kg. of coal fired there would have to be introduced 7.66 kg. of air for theoretical combustion.

The length of the burn was 204 hours.

The coal consumption per hour is shown in Fig. 6 for each period of 12 hours throughout the burn. Fig. 7 gives the time-temperature curves for the kiln (couple introduced on top) and the flue as well as the draft gauge readings. The latter are taken from the stack, and it must be remembered that each division equals $\frac{3}{4}$ inch and that the readings are magnified four times. Each division thus corresponds to 3-16 inch of petroleum, vertical height. In Fig. 8 the CO_2 and air contents of the gases are represented. From the air curve we observe that the shale is not a difficult one to oxidize, that the air content of the gases is not excessive, and the heat losses are not so much due to large air excess as to the high exit temperature of the waste gases.

FIG 8.
PAVING - BRICK KILN.
AVERAGE CARBON DIOXIDE
&
AIR CONTENT OF FIRE GASES.



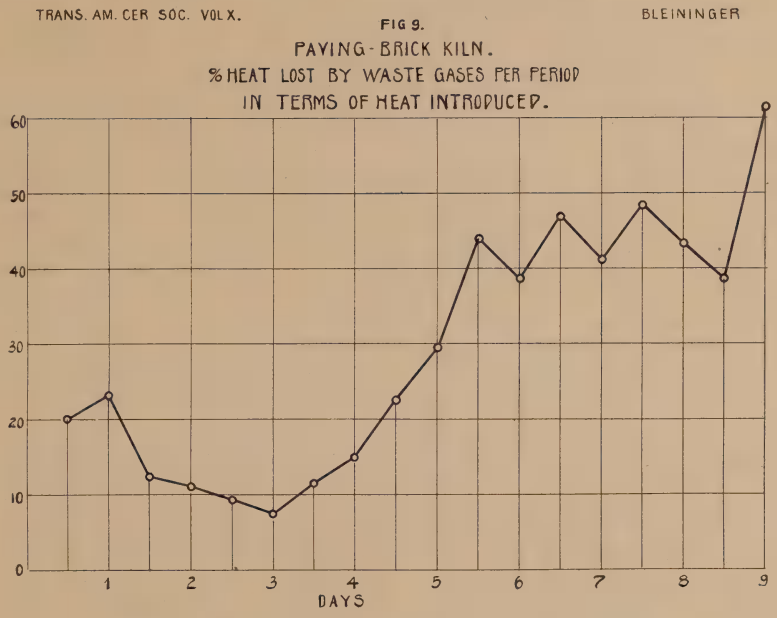
HEAT CARRIED OUT BY WASTE GASES.

Proceeding as before we can calculate the heat carried out into the flue from the weight of coal fired per period, the air content of the gases and the flue temperature, so that we have the following results:

Period	1	2	3	4	5	6	7	8	9
Kg. calories lost per kg. of coal	1237	1428	797	698	564	466	719	938	1408
% of heat lost in terms of heating value of coal	19.85	22.92	12.8	11.21	9.05	7.48	11.54	14.7	22.60
Pounds of coal lost by waste gases per period	156	305	171	307	518	645	995	1355	2001

Period	10	11	12	13	14	15	16	17	18
Kg. calories lost per kg. of coal	1847	2685	2390	2875	2561	3005	2653	2400	3839
% of heat lost in terms of heating value of coal	29.63	43.09	38.36	46.14	41.10	48.20	42.58	38.53	61.61
Pounds of coal lost by waste gases per period	2693	3174	3366	4122	3516	2472	3970	3804	2884

Adding the pounds of coal, which are equal to the heat wasted by the fire gases, we obtain 36,454 pounds, which is 29.9% of the total amount of coal fired, or we may say that the kiln shows a flue loss of 29.9%. Fig. 9 shows the heat loss per period graphically.



HEAT REQUIRED IN HEATING UP THE WARE.

Calculating the amount of heat theoretically necessary to raise the clays to 1110°C, as shown above, we find that this heat is equal to 13,778 pounds of coal, which is 11.3% of the total amount.

HEAT LOST BY UNBURNT CARBON IN THE ASHES.

Since the carbon lost by the ashes is equal to 3.03% of the coal, the heat lost in this way must be equal to $8080 \times 0.0303 = 245$ calories, or 3.9% of the calorific value of the coal.

HEAT TAKEN UP BY THE KILN AND LOST BY RADIATION.

This necessarily must be equal to 100 − 45.1 = 54.9%.

Summarizing, we have the following heat distribution:

Heat lost by the waste gases	29.9%
Heat taken up by the brick	11.3%
Heat lost by carbon in the ash	3.9%
Heat taken up by the kiln and lost by radiation	54.9%
	100.0%

In this kiln and under the conditions of the test carried on

1000 kg. burnt clay required 2056230 kg. calories.
1 ton burnt clay required 1871169 kg. calories.
1 ton burnt clay required 660 pounds of coal.
Temperature 1110°C.

TERRA COTTA KILN. A.

This kiln was a muffle kiln, the muffle being 16 ft. in diameter. The kiln was set with 42,423 pounds of green terra cotta and 26,960 pounds of supports, kiln blocks, etc. The coal consumed was 29,340 pounds, and the duration of the burn was 67 hours. The maximum temperature reached in the muffle was 1080°C.

Coal analysis:

Carbon	66.78%
Hydrogen	4.81%
Sulphur	0.84%
Oxygen and Nitrogen	9.68%
Ash	7.59%
Moisture	10.30%

Calorific power 6716 or 12090 B. T. U.

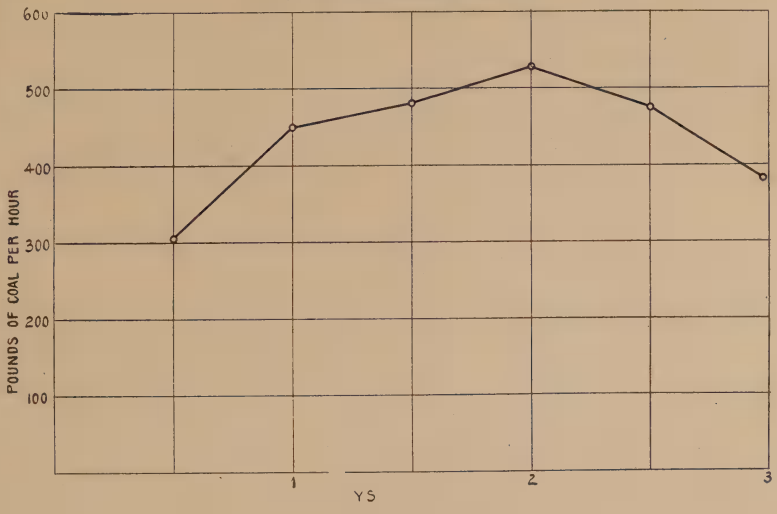
Analysis of ashes:

Carbon	20.92%
Hydrogen	0.06%
Sulphur	0.35%
Oxygen and Nitrogen	0.53%
Ash	77.94%
Moisture	0.20%

Assuming theoretical combustion, the weight of the gases developed from 1 kg. of coal is 2.39 kg., carbon diox-

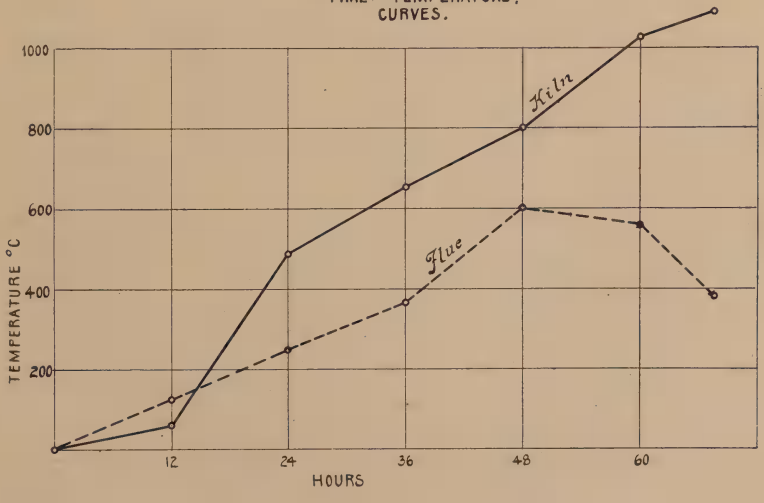
TRANS. AM CER SOC. VOLX BLEININGER

FIG 10.
TERRA COTTA KILN A.
COAL CONSUMPTION PER HOUR.



TRANS. AM CER SOC VOLX. BLEININGER

FIG 11.
TERRA COTTA KILN A.
TIME ~ TEMPERATURE, CURVES.



ide, 0.553 kg. steam, and 5.8 kg. nitrogen, the sulphur being neglected. The air introduced under the same conditions would be 7.54 kg.

Fig. 10 shows the average coal consumption per hour for each period of 12 hours. It is seen to differ from the corresponding curve for the open kilns by the comparatively small fluctuations in the amounts of fuel fired, as is to be expected from this type of kiln. The time-temperature curve is given in Fig. 11. The CO_2 and air curves of

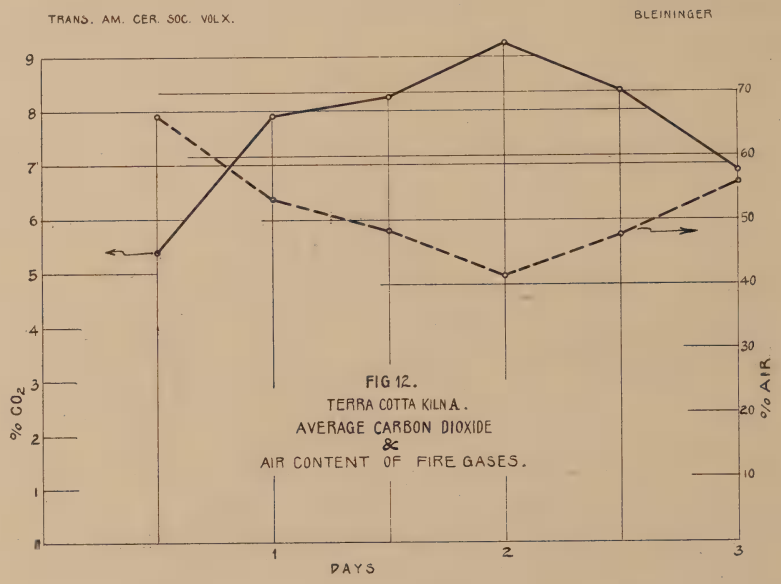


Fig. 12 indicate strongly oxidizing conditions throughout the burn. The draft gauge readings have been rejected owing to the rather unsatisfactory place at which the gauge was connected to the flues surrounding the muffle.

HEAT CARRIED OUT BY THE WASTE GASES.

Proceeding with the calculation of the flue loss we can tabulate the results as follows:

Period	1	2	3	4	5	6
Kg. calories lost per kg. of coal	741	1102	1476	1954	2622	2510
% of heat lost in terms of heating value of coal	11.0	16.4	22.0	29.1	39.0	37.4
Pounds of coal lost by waste gases per period	396	876	1248	1830	2214	1017

Adding up the amounts of coal we have 7581 pounds, which is 25.8% of the total amount of fuel used, 29,340 pounds. In Fig. 13 the average heat losses per period are shown graphically.

HEAT REQUIRED TO BURN THE WARE.

Calculating the heat theoretically required to burn the terra cotta and to heat up the supports, we find that this amounts to 3,688 pounds, or 12.57% of the total heat introduced.

HEAT LOST BY CARBON IN THE ASHES.

The carbon lost with the ashes amounts to 1.6% of the coal. Thus the heat lost in this way is $(8080 \times 0.016) \div 6716 \times 100 = 1.9\%$. In this kiln the grates were in excellent shape, and this explains the low loss.

HEAT TAKEN UP BY THE KILN AND LOST BY RADIATION.

It is evident, then, that the loss must be equal to $100 - (25.8 + 12.57 + 1.9) = 59.73\%$.

Summarizing, the heat distribution is as follows:

Heat lost by waste gases	25.80%
Theoretical heat necessary to heat up charge	12.57%
Lost by carbon in the ashes	1.90%
Heat taken up by kiln and lost by radiation	59.73%
	100.00%

1000 kg. terra cotta under these conditions required 5113775 kg. cals.=1675 pounds of coal.

1000 kg. terra cotta plus supports: 3007205 kg. cals. =985 pounds of coal.

1 ton terra cotta required 1524 pounds of coal.

1 ton terra cotta plus supports 896 pounds of coal.

Temperature=1080°C.

In taking several samples of gas from the muffle during the raising of the heat, 3% of CO_2 were found.

TERRA COTTA KILN. B.

This kiln was constructed entirely differently from the preceding one. Its inside muffle diameter was 21′6″, its height 17 feet high in the center and 12 feet to the spring of the arch. The charge consisted of 113,280 pounds of terra cotta and 75,694 pounds of kiln stones and supports. The fuel used amounted to 81,420 pounds of coal. Length of burn, 115 hours. The kiln was well built and in excellent condition. The maximum temperature was 1115°C.

Analysis of coal:

Carbon	69.30%
Hydrogen	4.62%
Sulphur	1.64%
Oxygen and Nitrogen	9.94%
Ash	6.55%
Moisture	7.95%

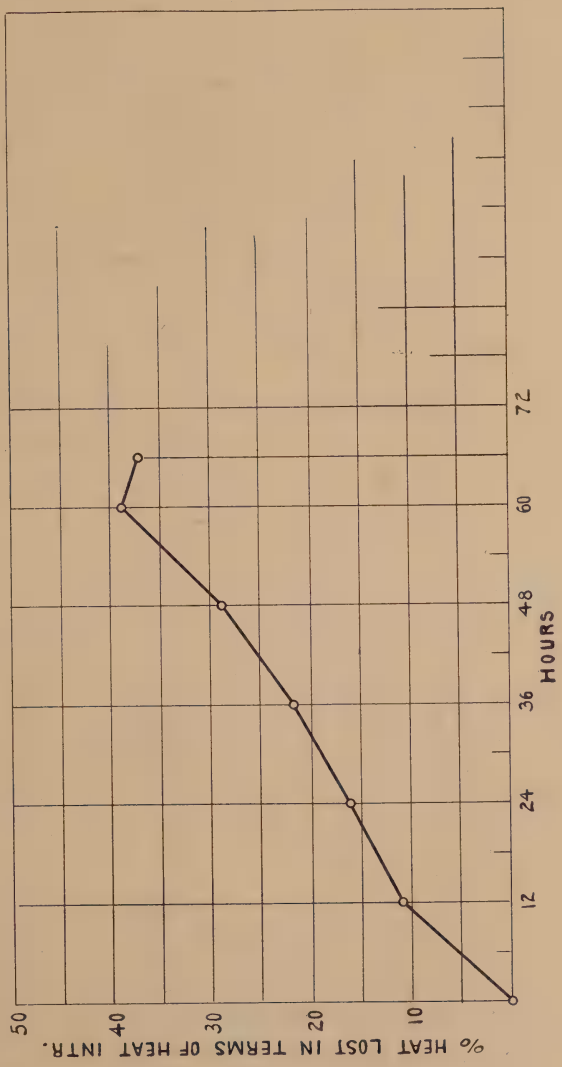
Calorific power 6961, or 12530 B. T. U.

Analysis of ash:

Carbon	20.53%
Hydrogen	0.22%
Sulphur	0.51%
Oxygen and Nitrogen	1.03%
Ash	77.40%
Moisture	0.31%

1.34% of carbon was lost in the ashes. 1 kg. of coal resulted in 2.49 kg. carbon dioxide, 0.495 kg. of steam, and 6.97 kg. nitrogen, assuming theoretical combustion, and 1 kg. of coal required under these conditions 8.24 kg. of air for combustion.

FIG 13.
TERRA COTTA KILN A.
% HEAT LOST PER PERIOD BY WASTE
GASES IN TERMS OF HEAT INTRODUCED.



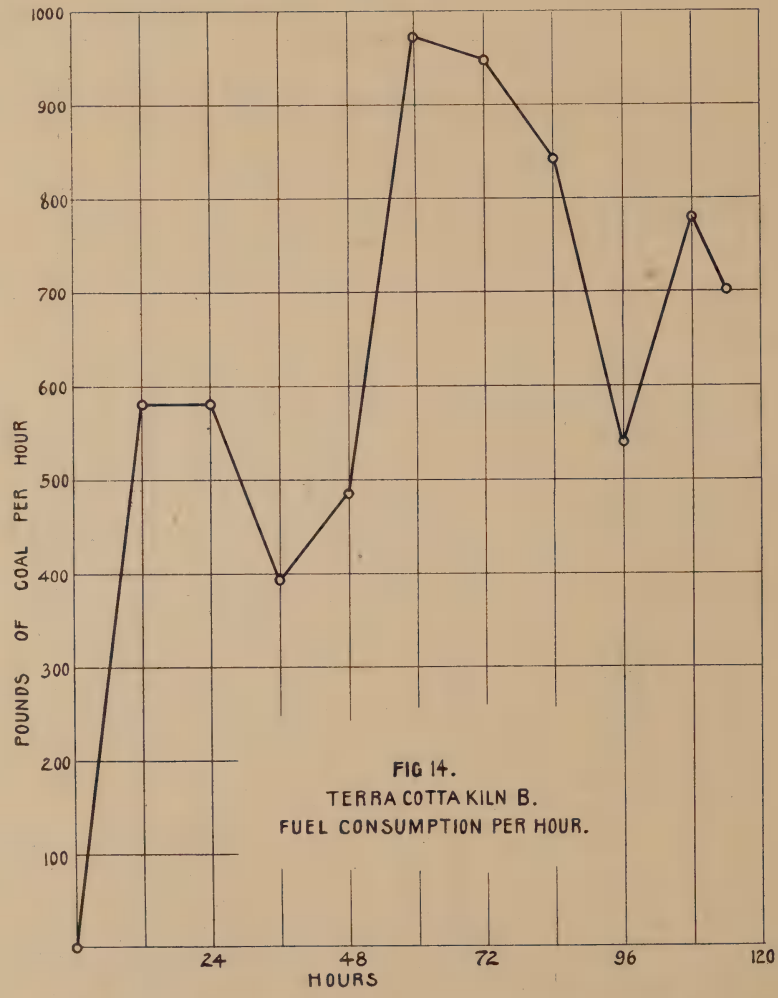
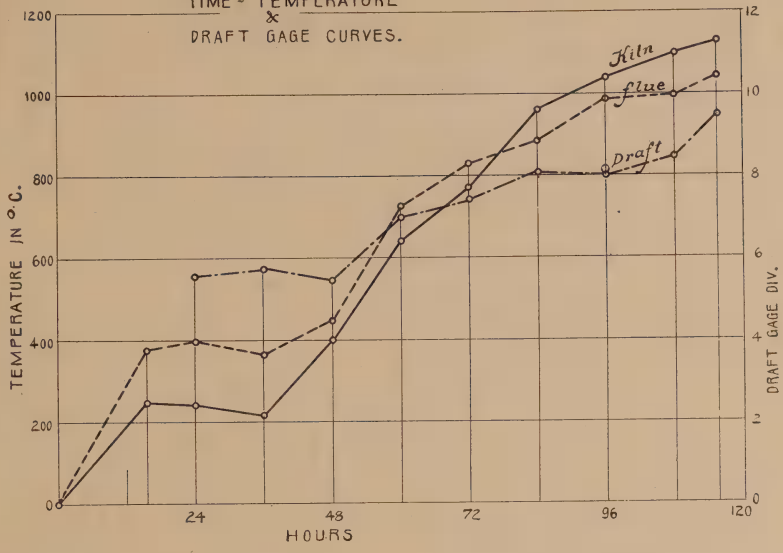


FIG 14.
TERRA COTTA KILN B.
FUEL CONSUMPTION PER HOUR.

Fig. 14 shows the coal consumption per hour as the average for each period of 12 hours. In Fig. 15 we have the time-temperature curves for the kiln and the flue as well as the draft gauge readings. It is shown here that the fire gases leave at a very high temperature and that hence a large flue loss is to be expected. The difference

TRANS AM. CER. SOC. VOLX. BLEININGER

FIG 15. TERRA COTTA KILN B.
TIME - TEMPERATURE
&
DRAFT GAGE CURVES.



TRANS. AM. CER SOC. VOLX. BLEININGER

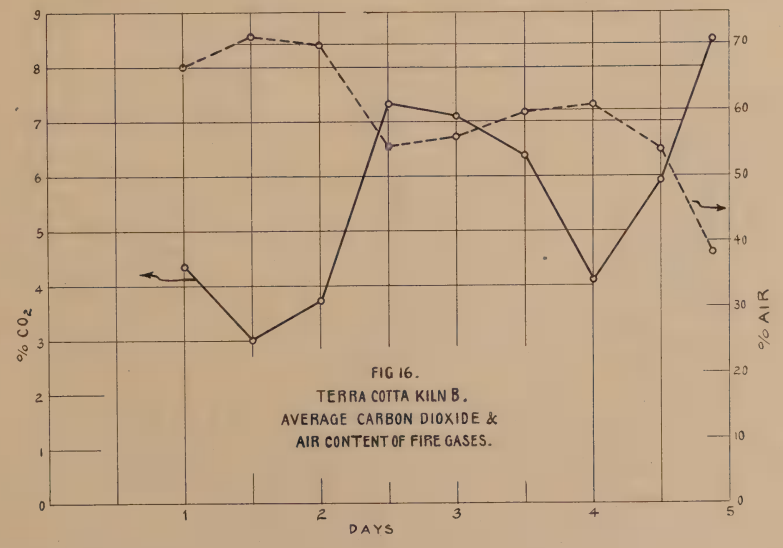
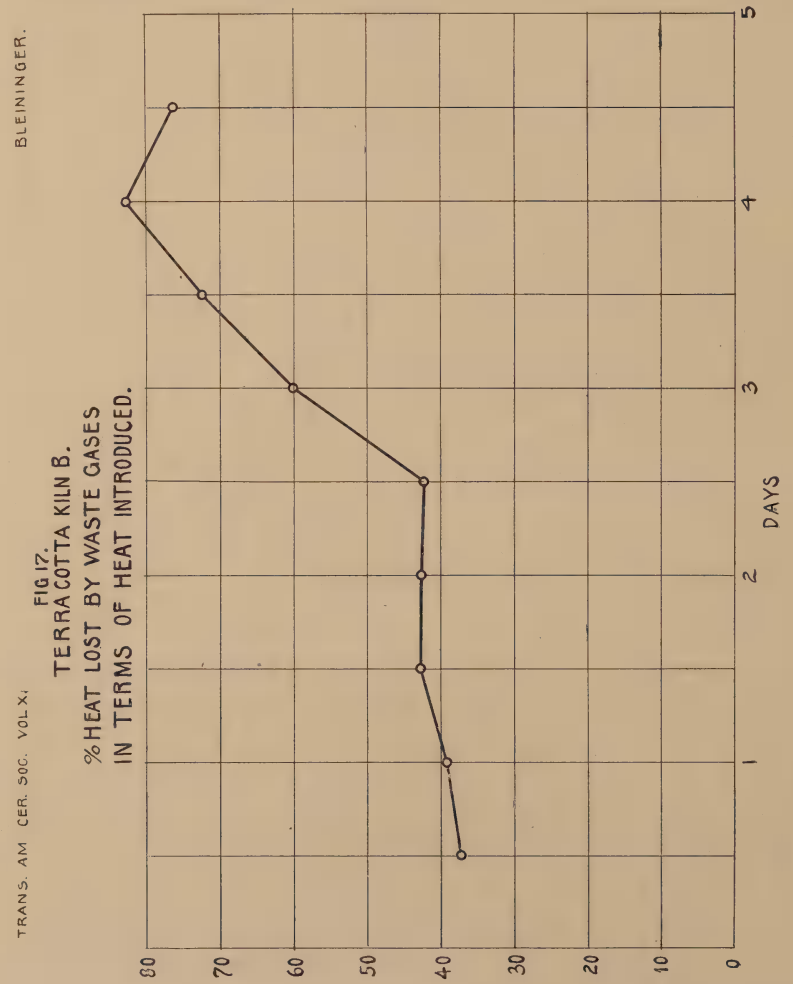


FIG 16.
TERRA COTTA KILN B.
AVERAGE CARBON DIOXIDE &
AIR CONTENT OF FIRE GASES.

in construction between kilns A and B is brought out clearly by these curves. Fig. 16 illustrates the average carbon dioxide and air contents of the fire gases representing for each period. It is observed that in this kiln also the conditions are decidedly oxidizing.

HEAT LOSSES DUE TO THE FLUE GASES.

The results of the calculations are again indicated in a table, viz:



Period	15½ hrs. 1	2	3	4	5	6	7	8	9	10
Kg. calories lost per kg. of coal	2576	2704	2992	3019	3007	4155	5031	5762	5281	4387
% of heat lost in terms of heating value of coal	37.0	38.8	43.0	43.4	43.2	59.7	72.3	82.8	75.9	63.0
Pounds of coal lost by waste gases per period	2581	2706	2044	2545	5000	6719	7335	5381	7099	5068

Fig. 17 shows the percentage of heat lost during each period.

Adding up these amounts of coal we find that the pounds of coal lost by the waste gases are equal to 46,478 pounds, or 57.1% of the total amount of coal, 81,420 pounds.

HEAT REQUIRED TO BURN THE WARE.

By calculation the theoretical amount of heat required to burn the terra cotta and heat up the supports was equal to 6514 pounds, or 8% of the total amount of coal.

HEAT LOST BY UNBURNT CARBON IN THE ASHES.

Since the carbon lost to the ashes amounts to 1.34%, the percentage heat loss due to this cause is $[(8080 \times 0.0134) \div 6961] \times 100 = 1.6\%$.

HEAT TAKEN UP BY THE KILN AND LOST BY RADIATION.

This is equal to $100 - (57.1 + 8.0 + 1.6) = 33.3\%$. This item, therefore, is very small for this kiln, which speaks well for its construction.

Summarizing, we have:

Heat lost by the waste gases	57.1%
Theoretical heat required for charge	8.0%
Heat lost by unburnt carbon	1.6%
Heat lost to kiln and radiation	33.3%

1000 kg. terra cotta required 5002518 kg. calories.
1000 kg. terra cotta and supports 3072423 kg. calories.
1 ton terra cotta required 1439 pounds of coal.
1 ton terra cotta and supports 884 pounds of coal.
Temperature 1115°C.

It will be observed that in spite of the large flue loss in kiln B and the higher muffle temperature the efficiency is about the same as that of A, this being due to the larger size and hence greater tonnage of B.

For the sake of completeness the writer desires to quote the results obtained for a brick kiln,* burning hard

*The *Clay Worker*, February, 1908.

shale building and sewer brick. This kiln was of the down draft type, 28 feet inside diameter, and contained 66,190 brick, each weighing 6⅛ pounds. The amount of coal consumed was 95,045 pounds, the B. T. U. value being 11162. The summary of the heat distribution of this kiln was as follows:

Heat lost by the flue gases	27.33%
Theoretical heat required to burn bricks	19.55%
Heat lost by unburnt carbon	3.51%
Heat taken up by kiln and lost by radiation	49.61%
	100.00%

1000 kg. of brick required 1,449,174 kg. calories, or for each ton of ware 468 pounds of coal were fired. The temperature was 1100°C.

Comment on the work of this article is hardly necessary since the figures themselves are the conclusions to be drawn. It might facilitate comparison to arrange the absolute quantities of heat required in each case.

1000 kg. sewer-pipe	4378341 kg. calories
1000 kg. paving brick	2056230 kg. calories
1000 kg. terra cotta, A	4640756 kg. calories
1000 kg. terra cotta plus supports	3007205 kg. calories
1000 kg. terra cotta, B	5002518 kg. calories
1000 kg. terra cotta plus supports	3072423 kg. calories
1000 kg. hard building brick	1449174 kg. calories

Expressing these values in pounds of coal per ton we have:

1 ton sewer pipe	1457 pounds coal
1 ton paving brick	660 pounds coal
1 ton terra cotta, A*	1524 pounds coal
1 ton terra cotta and supports	896 pounds coal
1 ton terra cotta, B	1439 pounds coal
1 ton terra cotta and supports	884 pounds coal
1 ton building brick	468 pounds coal

In conclusion the writer wishes to acknowledge his indebtedness to Professor C. W. Rolfe for having granted the use of the funds and apparatus which made the work possible. He also desires to express his appreciation of the conscientious services and faithful cooperation of Mr. C.

*The coal used in A is inferior in heating value to that in B.

E. Merry, of the department of ceramics, University of Illinois. He wishes to thank especially the firms whose kind ooperation was enjoyed in every case.

DISCUSSION.

Mr. Langenbeck: I wish to ask about the percent loss of waste gases—I presume by that the speaker means both the lost heat of the gases during the combustion of the kiln and the heat loss by radiation, not only from the outside during the burning, but also during the cooling of the ware through the stack. Did you attempt in any way taking the temperature on the outside of the kiln at the various points and times to determine what the percent of this loss was, this radiation of the kiln shell during the combustion?

Mr. Bleininger: I have made no attempt to do this since this is a very difficult matter, no reliable data being at hand to serve as the starting point of such calculations. The German Government is endeavoring to obtain the necessary facts by experimental researches. There is absolutely no reliance to be placed on any data found in handbooks concerning radiation. There are any number of theoretical calculations on this subject, but they do not agree in their deductions.

Mr. Langenbeck: I am glad the German Government is investigating this, for it is a matter of vital importance. Firing a kiln is piling up heat in its shell, and we usually think only that the inflow must be greater than the outflow. At the same time a large and increasing amount of heat is being radiated on the outside; and while, relatively, fire brick work is a poorly conducting substance, yet it is by no means as poor as it ought to be; and this is one of the gross defects of our kilns. We simply go on building kilns of fire brick instead of more effective insulating material, instead of using hollow brick. The saving, entirely, aside from the possible saving in fuel, is in the steadier accumulation of heat in the kiln by a lessened radiation from the

outside. The only larger practical work I have attempted along this line was in building a kiln at the Mosiac Tile Co., in Zanesville, Ohio, where I left an air space between the fire brick lining and red brick outside, and I held the fire brick lining in place by a header brick which extended an inch or an inch and a half beyond the red brick. But I was not able to follow it up properly and cannot give you any data, because the question is too difficult, as Mr. Bleininger says, and it was a very insignificant trial to make. But I believe if pottery companies will make up their minds to pay a little more for hollow fire brick and put up their kilns of them, it will be worth while.

Another question I wish to ask. In pointing out the loss of fuel in firing, in the beginning, Mr. Bleininger says that it is necessarily much greater than in a boiler. Is that your idea?

Mr. Bleininger: Yes, sir, not in the beginning so much as later on.

Mr. Langenbeck: I can understand that the greater the temperatures the greater the loss by radiation and gases might be, but your statement might be subject to the misinterpretation, as that a high temperature apparatus like a kiln is more wasteful in its work than a low temperature apparatus like a boiler. When we introduced gas at the Mosaic Tile Co., it proved more economical to fire our kilns with gas than with coal but not our boilers, and we returned to coal for firing the boilers. The kiln as an apparatus is much more economical of fuel, in my experience, measured by dollars and cents, than boilers, because the latter in its work chills the fire gases below the combustion temperature, the former does not.

Mr. Bleininger: I was referring to the effect produced. In the boiler you are getting effect measured by water evaporation; in the kiln, by the burning of the ware to a certain temperature. From this standpoint it is more economical than the kiln.

Mr. Langenbeck: I wanted to bring out what might be misinterpreted in that point.

Mr. Wheeler: We certainly are deeply indebted to Mr. Bleininger for this very valuable contribution, showing what we do not know. He has put a magnificent amount of work there, and the facts are very clearly and concisely stated.

I will ask one question to bring out one point more clearly. Were those kilns selected under normal conditions, with the common, everyday firing, or were they specially fired by expert workmen, and was there any handling of the kilns? I will also ask Mr. Bleininger, in that loss which he ascribes to radiation and kiln loss, whether he attempted to roughly differentiate between the external shell loss and what might be safely deducted as not external radiation? If he could give us a hint on that it would be greatly appreciated.

Mr. Bleininger: I have not attempted to do this. But in one case where the conditions were favorable, where the air was being drawn out of the kiln by a fan, we attempted to measure the heat retained in the kiln. We inserted a pyrometer and later on thermometers into the goose-neck, and knowing the pressure exerted by the fan we were able to roughly calculate the velocity. I have not finished the work, but we shall be able to calculate the weight of the air and the temperature, and therefore roughly the heat taken by the fan from the kiln. In other plants the conditions have not been favorable.

Answering the first question, I will say that the conditions were the ordinary conditions, no expert help being employed. I asked the superintendents to take no special precautions, but to let things go on in their usual way. Mr. Merry can tell us how he found conditions.

Mr. Merry: As to whether the kilns were the average or not, I think the sewer pipe kiln was the worst on the yard. The others were about the average kiln.

Mr. Aubrey: I will ask Mr. Bleininger what he calculates the heat retained by the ware? Is that heat taken to perform the mechanical action in the clay ware?

Mr. Bleininger: The calculated heat includes that

required for the expulsion of the mechanical water, the raising of the heat of the clay itself from the atmospheric temperature to the final temperature, and that taken by the expulsion of the chemical water. We have no accurate figures in regard to the heat of decomposition of the hydrous clay substances. I have assumed it to be 200 calories per gram of such water.

THE FUNCTION OF ALUMINA IN A CRYSTALLINE GLAZE.

BY

WOLSEY G. WORCESTER, Columbus, Ohio.

In studies on crystalline glazes, and in articles that have appeared in the transactions of this society and in the various trade journals from time to time, the writer has noticed that in almost every case, our American investigators as well as the French, have used a type of glaze in which aluminum oxide is absent, while most German formulæ call for its use.

It has also been observed that 0.05 equivalents aluminum oxide appears to be the amount that our German co-workers use most frequently.

Seger* says that the introduction of alumina to a glaze has a tendency to obviate the faults that are to be expected in a glaze free from alumina, i. e., tendency to devitrification, and the running off or soaking in of the glaze.

Langenbeck† says that it is the alumina and similar elements which tend to keep the glaze from devitrification in the protracted glost-fire.

Why do the Germans use alumina in their glazes? Is it to promote the growth of crystals, or to produce a certain type, or for mechanical reasons, such as producing less flow in the molten glaze or causing the glaze ingredients to float better and stick to the body more strongly, without dusting?

After diligent search to find data on the question, and failing, the writer decided to study the real function of alumina in a crystalline glaze.

In a few short experiments it has been the object to

*Vol. II, p. 570. †Chemistry Pottery, p. 51.

try and show, if possible, whether alumina hinders or promotes the growth of crystals.

PRELIMINARY STUDY OF HEAT TREATMENT.

Realizing that it would be unwise to start upon this investigation without first studying the heat treatment required for glazes of this type, and proving that such glazes could be reproduced from time to time with some degree of certainty, four glazes were taken as standards, not for any special reason other than that they had all produced crystals of good size and shape.

The heat treatment for three of these standard glazes was known, while as to the fourth, nothing but the percent of composition could be obtained.

The glazes were as follows:

1	.3 Na_2O .7 ZnO	1.5 SiO_2*
2	.4 K_2O .6 MnO	.75 SiO_2*
3	.33 KNaO .66 ZnO	1.24 SiO_2* .29 TiO_2
4	.30 K_2O .70 ZnO	1.70 SiO_2† .29 TiO_2

In the case of No. 2, the black oxide of manganese was used, but by later information it has been learned that Purdy used the carbonate. This explains the failure to reproduce his type of crystals in the glaze of the same formula.

In the case of No. 3 0.15 of the KNaO was from KNO_3, while 0.18 was from Na_2CO_3.

The titanium for this work was furnished by the Foote Mineral Co., of Philadelphia. Two grades being used, one known as their Ceramic Iron-free Rutile, the other, as Standard Ruby Rutile, or TiO_2. As to the results obtained by the use of either grade, the writer has been unable to detect any difference.

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*Purdy, Trans. American Ceramic Society, Vol. IX, p. 378, 380, 400.
†Gates, Trans. American Ceramic Society, Vol. VII, p. 44.

After weighing out and mixing the various ingredients for each glaze, the entire batch of each glaze was placed in a large-size Hessian crucible, and fritted, one at a time, in a pot furnace fired with natural gas and compressed air.

The fritting was allowed to proceed until bubbling had ceased, and the fritt could be easily poured out of the crucible into a bucket of water. The fritt was then placed in a ball mill and ground until it easily passed a 150 mesh sieve.

Each glaze was now put into pans and evaporated to dryness, passed through an 80 mesh sieve several times to insure an even mixture, and was then put into glass jars for use.

When ready to prepare trials, a small amount was taken out into a saucer and worked up with a gum tragacanth solution to a thick slip. Then by means of a soft brush it was applied to 1½x3 inch vitrified white tiles in a thick coating.

The trial pieces were now placed in small setters, and when ready to fire it was deemed best to use a coke-coal fired kiln, to folow as closely as possible the temperature curve of Purdy*

A pyrometer was used, and with only slight variations Purdy's curve was reproduced very closely up to the maximum temperature of 1200 C., but our kiln being of a small up-draft type, the cooling could not be followed at the proper rate.

Results of Burn 1.

Glaze No. 1 had become bright and clear, with two small star-like crystals of the common variety produced by zinc glaze, and about ⅛ inch in diameter.

Glaze No. 2 had produced the best crystals of the burn. They were of several forms, the most pronounced being as per cut No. 1.

*American Ceramic Society, Vol. IX, p. 336.

CUT IV. SHOWING TILE WITH ZINC SILICATE CRYSTALS.
GLAZE №2.500 CONE 1-2.

SHOWING MANGANESE CRYSTALS. GLAZE 2, BURN 1.

All were black with an iridescence over most of the surface.

Glaze No. 3 gave very slight traces of crystals of the typical fan-shape variety produced by zinc where the glaze had run thin.

Glaze No. 4 gave results similar to No. 3.

The conclusions drawn from this burn seemed to indicate that while the glazes did not crystallize in a very marked way, they gave good indications of crystals at least.

The heat treatment, or rather the cooling treatment, had not been conducive to the best growth of crystals. And further, it was thought necessary to use a kiln in which the cooling could be conducted slower or, if found necessary, the rate of cooling could be changed from time to time. It was also noted that the glazes had given the best indications of crystallizing where they had run most freely.

In order to correct the cooling conditions, a second burn was now undertaken; it was thought best to apply the glaze on vases as well as flat surfaces, in order to encourage flow.

When the trials were ready they were placed in ordinary saggers, which had been washed with a raw lead glaze inside, and were fired in a "Revelation" kiln equipped with natural gas for fuel instead of oil.

Purdy's curve was again closely followed, and the rate of cooling was regulated by shutting off a small amount of the gas supply at intervals of each hour, until it was thought that the glaze had cooled to a point where the crystals could not longer grow.

Results of Burn 2.

This burn proved more satisfactory than the previous one by producing more and larger crystals.

In the zinc type, glaze No. 1 applied on a small vase gave numerous star-like crystals of snow whiteness floating in a clear colorless matrix. Where applied on small individual butter plates, it produced a matted mass of

fine needle crystals, some threee-fourths of an inch long.

In glaze No. 2 a more pronounced type of the manganese crystal was obtained.

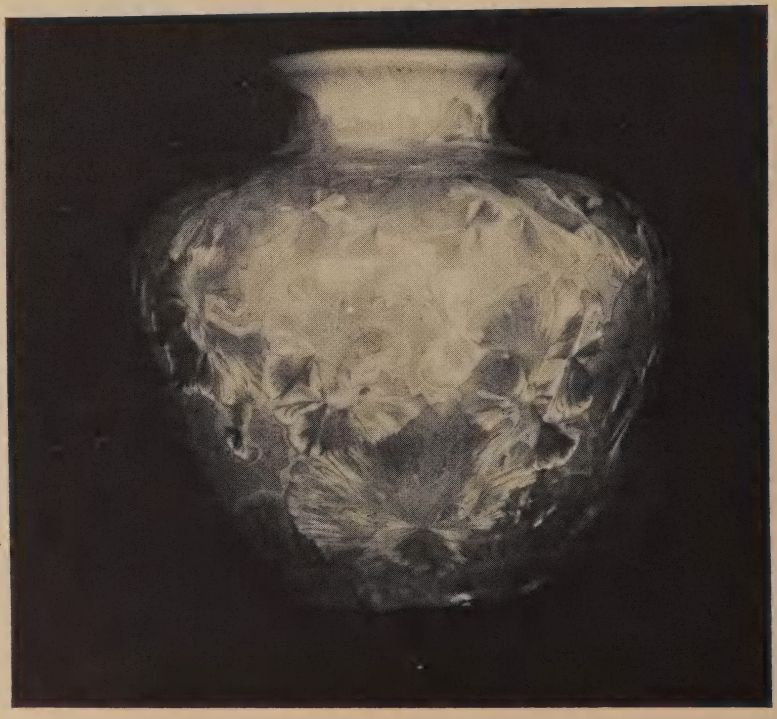
In Nos. 3 and 4 representing the zinc-titanium mixture, a nice showing of crystals was produced, which presented the appearance of having been dwarfed or stunted in their growth, possibly by cooling too fast at the point where development takes place.

It was evident that some condition necessary to the growth of the crystals had not yet been produced, and hence the growth of the crystals was still rather feeble.

Riddle's cooling curve,* and Mellor's,† shows that there should be a period during the cooling where the crystals develop the best, and that if the proper time or temperature could be found in the present instance it would only be necessary to hold the heat at that point until the crystals had attained their best growth, and then cool in the ordinary way.

This was accomplished by burning up to the point where the glaze was very fluid and then cooling slowly, drawing trials at intervals of about every 25°C until the point was reached where the crystals began to appear. The heat was allowed to drop another 25 degrees rather

*Trans. American Ceramic Society, Vol. VIII, page 345.
†Trans. English Ceramic Society, Vol. V, page 89.



quickly, the writer thinking that a slow cooling at the point where the crystals begin to appear or form would have a tendency to start too many of them growing. So it was deemed best to cool quickly at this point, only allowing a few crystals to start and then cool slow, allowing them to grow. This was carried out as near as possible, with the following results:

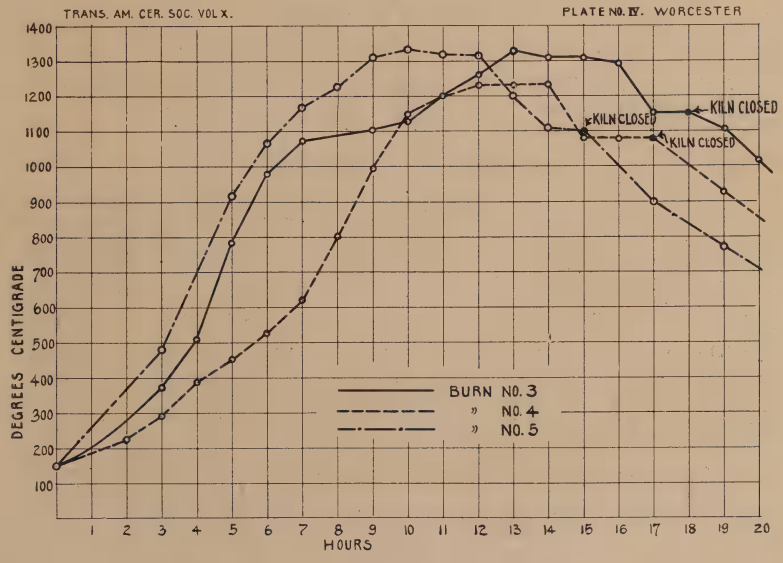
Results of Burn 3.

Glaze No. 1 on a vase produced a fine large crystallization over the entire surface.

Glaze No. 2 did not develop crystals to any great extent, but some very interesting specimens of the three pointed star-type and of larger size than before were obtained.

Glazes Nos. 3 and 4 were applied on a small butter dishes, and developed into a mass of perfect fan-shaped crystals, the coloring and luster of which were very beautiful. The color was a dark straw yellow, with borders of reddish material around the crystals of No. 4.

Also see curve for this burn marked No. 3 on plate No. IV.



Results of Burn 4.

A fourth burn was now made, at a final temperature 100°C lower than No. 3, thinking that possibly it would not be necessary to go so high. The cooling was varied somewhat, dropping a little lower from the finishing heat and then holding the temperature two hours instead of one.

The results of this burn, marked 4, plate V, were not to be compared with those of burn No. 3 for beauty. There were well formed crystals, but they lacked the sparkle of those of the previous burn.

The lesson drawn from this burn was as follows:

In a glaze of this type it is necessary to carry the burn to such a point that the glaze becomes very fluid, in order that all material in the glaze may come to a state of complete solution, then, when the cooling takes place, the crystallizing ingredients can easily separate from the balance of the glaze, and continue to grow until they are used up, or the temperature has dropped to a degree where the glaze stiffens to a condition where further growth is impossible.

It will be seen that in the case of crystal glazes on vertical walls, that it is very necessary to cool very rapidly for a short time after the maximum temperature has been reahed, in order to prevent the glaze from draining off the ware completely.

Results of Burn 5.

It was thought advisable to carry out another burn similar to No. 3, to see if the results could be duplicated. About the only difference in the two burns was in the time consumed in reaching the highest temperature, burn No. 5 taking about three hours less in reaching the maximum temperature. It had been the opinion of the writer that it did not make very much difference on a glaze of this type as to the time of heating up.

The results of burn No. 5 were in every way similar to No. 3, the crystals being of good size and well developed.

CRYSTALLIZATION EXPERIMENTS WITH ADDITION OF ALUMINA.

It was now thought that the real work could be undertaken, as the composition and habits of growth of four glazes was pretty well established.

A small series was planned, Table I, to show if possible what the nature of the effect of alumina would be on a zinc-titanium glaze.

TABLE I.

No.	K_2O	ZnO	Al_2O_3	SiO_2	TiO_2	Remarks
A	0.30	0.70	0.00	1.70	0.24	All Fritted
A-1	0.30	0.70	.01	1.70	0.24	
A-2	0.30	0.70	.02	1.70	0.24	
A-3	0.30	0.70	.03	1.70	0.24	
A-4	0.30	0.70	.04	1.70	0.24	From No. 4 and A-10
A-5	0.30	0.70	.05	1.70	0.24	Blended
A-6	0.30	0.70	.06	1.70	0.24	
A-7	0.30	0.70	.07	1.70	0.24	
A-8	0.30	0.70	.08	1.70	0.24	
A-9	0.30	0.70	.09	1.70	0.24	
A-10	0.30	0.70	0.10	1.70	0.24	All Fritted

As will be seen by the table, this series was prepared by fritting the two extremes and then blending the intermediates.

The A-10 fritt was exceedingly hard to fuse, in fact, it did not come a point beyond a good slag of a stony nature.

After thoroughly blending these glazes they were applied to small vitrified porcelain tile and fired in the usual way, following the curve of burn No. 3, as near as possible.

Results.

By referring to the cut, Fig. 5, it will be seen that glaze A-1 has produced at one end of the tile fan crystals of good size. No difference can be seen between the crystals on this trial piece and those of the regular zinc-titanium type.

A-2 had changed very materially from the regular fan type.

Instead of having a growth of a few fan crystals the entire surface of the tile is made up of needle crystals, very fine and greatly interwoven one with another.

A-3 is very much the same as A-2 except that there are not so many crystals. The glaze matrix seems to be more dry and stony.

A-4. This glaze has the texture of a semi-matt, but is entirely free from any crystals so far as the eye can detect.

A-5-6-7-8 can be described together. They all present a semi-matt appearance, smooth to the touch, and have no signs of crystals. Their color is gray with tinges of yellowish green.

A-9. This glaze has semi-fused, but was evidently not soft enough to run smooth. There are still remaining in its surface small pits or bubbles. No signs of crystals are visible.

A-10. The glaze of this number is void of crystals, and while it is vitrified it is only glossy, and at one end of the tile it is dry and full of pin holes.

Conclusions.

This set of trials seem to show us that alumina has changed the type of crystal from that of fan shape to needle crystals.

Also that 0.04 alumina in the glaze has so changed it, most likely in a physial way, that further crystallization is impossible at the temperature used. It is not at all unlikely but what this entire series would develop crystals, if it were possible to attain the proper heats to produce fluidity of the glazes.

This burn, also, showed very clearly that it would be very inconvenient to take for the starting point of our future work glazes requiring such high temperatures to mature as those used up to the present time. (About Cone 12).

A new series was therefore planned, with the object

of producing a glaze, having a melting point low enough to enable us to use 0.1 alumina and still melt at Cone 10.

It was decided at this point in the work to devote the study to a simple zinc glaze in order not to have too many elements present at one time, that might affect the growth of the crystals.

A glaze was prepared of the following formula:

$$\left.\begin{matrix}.33\ NaO \\ .77\ ZnO\end{matrix}\right\} \quad 0.0\ Al_2O_3 \quad \left\{\begin{matrix}1.60\ SiO_2 \\ .20\ B_2O_3\end{matrix}\right.$$

And after fritting the entire batch, it was ground to pass a 150 mesh sieve, then evaporated to dryness and passed through an 80 mesh sreen several times to insure a proper mixture. A part of this mixture was made into a slip condition by the use of gum solution. Tiles were now prepared by applying the glaze with a brush.

At the same time a number of cones were made from the glaze. When the kiln was set three of these cones were placed where they could be watched, the idea being that when they melted down it would give a warning that our glaze was reaching maturity.

This occurred close to Cone 1. The temperature was maintained at this point, trials being drawn at intervals of one-half hour, and at the third draw, the glaze had become clear and fluid.

From this point, the kiln was allowed to cool rapidly for one hour. The temperature at the end of that time was held for another hour and the kiln was then closed.

Cut No. 6 shows the results of this burn very nicely. Crystals of fairly good size have been formed. It will be seen that around the edge of the tile we have a border of needle crystals, while the central area of the tile shows the star-type.

Taking into consideration the temperature at which this glaze matured, and the ease with which it developed crystals, it was thought safe to plan future work with this as a basis.

In considering the problem, the question arose as to

how the alumina would act, if derived from different sources. Hence a series was planned as follows:

$$\left.\begin{matrix}.33\ Na_2O \\ .66\ ZnO\end{matrix}\right\}\ 0.0\ Al_2O_3\ \left\{\begin{matrix}.20\ B_2O_3 \\ 1.60\ SiO_2\end{matrix}\right.$$

To

$$\left.\begin{matrix}.33\ Na_2O \\ .66\ ZnO\end{matrix}\right\}\ 0.1\ Al_2O_3\ \left\{\begin{matrix}1.60\ SiO_2 \\ .20\ B_2O_3\end{matrix}\right.$$

GROUP I.

No.	Na_2O	ZnO	Al_2O_3	SiO_2	B_2O_3	Remarks
520	0.33	0.66	0.1	1.60	0.20	All Fritted
518	0.33	0.66	0.09	1.60	0.20	
516	0.33	0.66	0.08	1.60	0.20	
514	0.33	0.66	0.07	1.60	0.20	
512	0.33	0.66	0.06	1.60	0.20	Alumina introduced from
510	0.33	0.66	0.05	1.60	0.20	clay which was fritted as a
508	0.33	0.66	0.04	1.60	0.20	part of the total batch.
506	0.33	0.66	0.03	1.60	0.20	
504	0.33	0.66	0.02	1.60	0.20	
502	0.33	0.66	0.01	1.60	0.20	
500	0.33	0.66	0.0	1.60	0.20	All Fritted

GROUP II.

No.	Na_2O	ZnO	Al_2O_3	SiO_2	B_2O_3	Remarks
540	0.33	0.66	0.1	1.60	0.20	All Fritted
538	0.33	0.66	0.09	1.60	0.20	
536	0.33	0.66	0.08	1.60	0.20	
534	0.33	0.66	0.07	1.60	0.20	
532	0.33	0.66	0.06	1.60	0.20	All alumina used in this
530	0.33	0.66	0.05	1.60	0.20	group was derived from the
528	0.33	0.66	0.04	1.60	0.20	oxide fritted as a part of the
526	0.33	0.66	0.03	1.60	0.20	batch.
524	0.33	0.66	0.02	1.60	0.20	
522	0.33	0.66	0.01	1.60	0.20	
500	0.33	0.66	0.00	1.60	0.20	All Fritted

GROUP III.

No.	KNaO	ZnO	Al_2O_3	SiO_2	B_2O_3	Remarks
560	0.33	0.66	0.1	1.60	0.20	All Fritted
558	0.33	0.66	0.09	1.60	0.20	
556	0.33	0.66	0.08	1.60	0.20	
554	0.33	0.66	0.07	1.60	0.20	
552	0.33	0.66	0.06	1.60	0.20	All alumina in this group
550	0.33	0.66	0.05	1.60	0.20	was derived from feldspar
548	0.33	0.66	0.04	1.60	0.20	fritted as a part of the batch.
546	0.33	0.66	0.03	1.60	0.20	
544	0.33	0.66	0.02	1.60	0.20	
542	0.33	0.66	0.01	1.60	0.20	
500	0.33	0.66	0.00	1.60	0.20	All Fritted

GROUP IV.

No.	Na_2O	ZnO	Al_2O_3	SiO_2	B_2O_3	Remarks
580	0.33	0.66	0.1	1.60	0.20	All alumina derived from
578	0.33	0.66	0.09	1.60	0.20	
576	0.33	0.66	0.08	1.60	0.20	
574	0.33	0.66	0.07	1.60	0.20	
572	0.33	0.66	0.06	1.60	0.20	clay added as a raw addition
570	0.33	0.66	0.05	1.60	0.20	to the fritted batch.
568	0.33	0.66	0.04	1.60	0.20	
566	0.33	0.66	0.03	1.60	0.20	
564	0.33	0.66	0.02	1.60	0.20	
562	0.33	0.66	0.01	1.60	0.20	
561	0.33	0.66	0.00	1.40	0.20	All Fritted

The above group, containing raw clay for the source of alumina, was made by preparing the following fritt, in order not to introduce too much silica upon the addition of the raw clay:

$$\left.\begin{matrix}.33\ Na_2O \\ .66\ ZnO\end{matrix}\right\} \quad 0.0\ Al_2O_3 \quad \left\{\begin{matrix}1.40\ SiO_2 \\ .20\ B_2O_3\end{matrix}\right.$$

After fritting, one-half of it was taken and to it was added .10 equivalent Al_2O_3 from raw clay, giving us the formula

$$\left.\begin{matrix}.33\ Na_2O \\ .66\ ZnO\end{matrix}\right\} \quad 0.10\ Al_2O_3 \quad \left\{\begin{matrix}1.60\ SiO_2 \\ .20\ B_2O_3\end{matrix}\right.$$

The clay was ground with the fritt in a ball mill until all passed a 150 mesh screen.

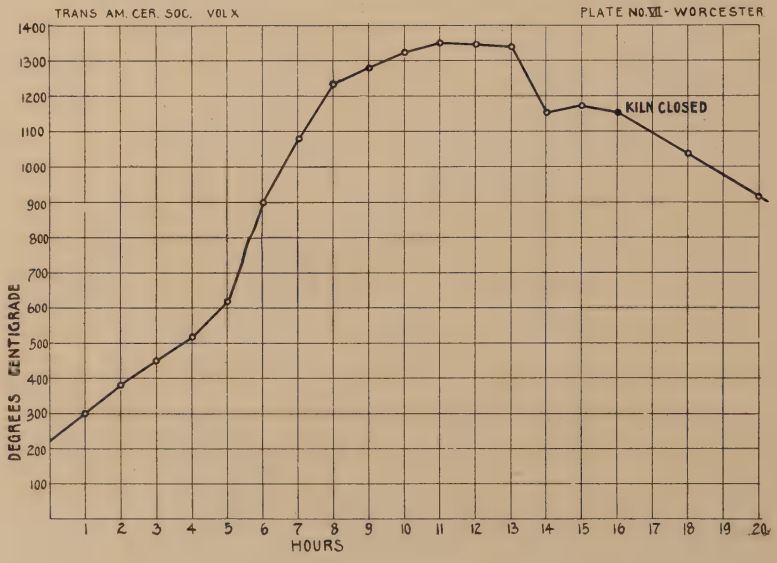
In making the blends for the four groups, the parts of each extreme were carefully weighed out and dry mixed, then made into a slip by the use of gum solution, and again mixed, producing what would seem to be a very intimate mixture.

These glazes were then applied to small 1½″x3″ white wall tile, by means of a brush, dipping having been found to be very difficult.

They were then placed in tile setters, holding eight tile each. The entire four groups were placed in the Calkin's Revalation kiln and fired with gas, giving the curve shown by Plate VII.

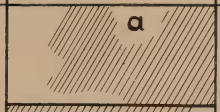
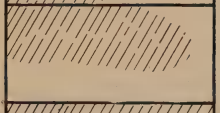
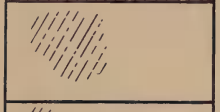
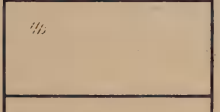
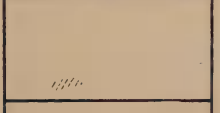
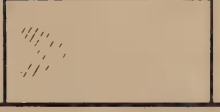
Results.

Group I. All alumina derived from clay fritted directly into the glaze, No. 500. This tile has an area of about one-fifth of its surface that is made up of fine needle crystals. The balance of the surface is a dry devitrified coating containing some large open bubbles near the edges.



GROUP I

CONTAINING Al_2O_3 FROM CLAY FRITTED WITH THE BATCH

No.		Al_2O_3	REMARKS
520		0.10	SOME VERY BEAUTIFUL STAR AND FAN-LIKE CRYSTALS AREA a IS COVERED WITH A SORT OF OPALESCENT ENAMEL.
518		0.09	TILE ALMOST COVERED WITH CRYSTALS, ONLY A SMALL CORNER OF SEMI MATT REMAINING.
516		0.08	SAME AS 512 EXCEPT THAT WHITE ENAMEL AREA IS LARGE. CRYSTALS ARE OF A FINE PEARLY LUSTER.
514		0.07	SMALLER AREA OF CRYSTALS BUT ARE VERY NICELY FORMED. BALANCE OF GLAZE RATHER ROUGH.
512		0.06	VERY BEAUTIFUL CRYSTALS ONLY SMALL AREA NOT COVERED ALSO HAS SMALL PATCH OF WHITE ENAMEL LIKE GLAZE.
510		0.05	LESS NUMBER OF CRYSTALS THAN 508 BUT LARGER. REST OF GLAZE SEMI-MATT
508		0.04	SOME WELL DEVELOPED BAR AND FAN-SHAPED CRYSTALS. BALANCE OF GLAZE NICE SEMI-MATT.
506		0.03	A NUMBER OF VERY NICE STAR CRYSTALS BLENDING OFF INTO FINE BAR-CRYSTALS. REST OF GLAZE SEMI-MATT.
504		0.02	SAME AS 502.
502		0.01	VERY SMALL AREA OF CRYST'S. BALANCE OF GLAZE BADLY BROKEN BY BUBBLES AND ABOUT A SEMI-MATT TEXTURE.
500		0.00	HAS SMALL AREA OF NEEDLE CRYSTALS, BALANCE OF GLAZE RATHER DRY AND HARSH BROKEN BY A FEW BUBBLES.

The small area of crystals gradually blends from crystals one-quarter inch long to smaller and smaller ones, which finally disappear in the devitrified coating. No doubt if this latter surface could be examined with a glass it would show crystallization.

No. 502.—Shows an irregular devitrified coating, badly broken by bubbles, more especially near the edges. On one tile there can be seen three small areas in which fine needle crystals are just breaking through the surface.

No. 504.—This number appears very much like 502, badly devitrified, showing a few small crystals. At the bottom of the larger bubbles can be seen needle crystals radiating like the spokes of a wheel.

No. 506.—At this point we reach a condition where the crystals, of a shape resembling the little flower known as Spring Beauties, appear. About one-third of one tile is covered with crystals. The balance of the tile is of a rough or crystalline surface. The other tile of this number shows but a faint sign of crystals, but the surface where not blistered has a fine soft matt finish, showing a slight dapple marking.

No. 508.—One tile in this set shows good crystallization over about one-third of its surface, the balance being of a soft matt nature. The other tile of this number is somewhat blistered, but the main surface of the tile is matt. Crystals only apear in the bubbles.

No. 510.—On both tiles of this number we have an area equal to about one-quarter of the tile, that has produed crystals of a size large enough to be seen. The balance of the tile has blistered slightly, but for the most part is matt.

No. 512.—One tile in this set has produced fine crystals over the entire surface, except for a very small area at one corner.

It can be seen that there is a border of fan crystals pointing inward, while the central area seems to be of a second or finer growth of crystals, very soft and closely

blended together. The other tile of this number has not developed crystals, at least not to the naked eye.

No. 514.—Both tiles of this number have developed crystalline areas equal to about one-half the surface. The crystals are well formed of the fan type. The rest of the surface is matt, but not so smooth to the touch as the ones lower in alumina.

No. 516.—One tile in this set has developed a large growth of crystals over all its surface, except a small portion at one end. This tile, like the one in 512, has a secondary growth of crystals. In the central part of the crystalline area there is to be seen a small space of white enamel-like material. This white substance, in the writer's

mind, is the same as that entering into the completed crystal, but the cooling dropped below the point where it could be absorbed by the growing crystals.

The other tile has its entire crystal portion made up of fine needle crystals, just breaking through the mass of glaze. The surrounding glaze is a fairly good matt.

No. 518—One tile of this number has developed a fine growth of crystals, all but one small corner of the tile being highly crystalline. The central area of this tile is made up of soft delicate crystals. The other tile has crystallized into large fan crystals over about one-third of its surface, the balance being matt.

No. 520.—Both tiles in this case have developed good crystals, one somewhat better than the other. The tile represented in the cut shows an area of about three-fourths of a square inch, that is made up of the white enamel-like material, spoken of before.

The area of the other tile not covered by crystals is of a rough matt texture.

Conclusions.

The conclusions to be drawn from this group as a whole seems to point to the fact that aluminum oxide in amounts of .03 equivalents up to 0.1 equivalents at this temperature, Cone 10, is beneficial, either in promoting the growth of the crystals, or, in holding the glaze from devitrifying and becoming dry.

The best crystals appear in Nos. 512, 514, 516, 518, 520, with 518 showing about the best distribution of crystals.

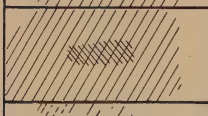
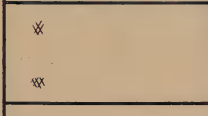
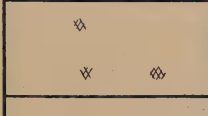
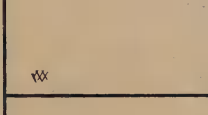
Group II. Alumina derived from aluminum oxide fritted into the glaze.

No. 522.—On one tile this glaze has become a dry devitrified coating, badly blistered, but in a number of broken bubbles a few needle crystals can be seen.

The other trial shows a much smoother surface, with only a few bubbles, while at several points on the surface

GROUP II

CONTAINING Al_2O_3 FROM ALUMINUM OXIDE FRITTED WITH THE BATCH.

NO.		Al_2O_3	REMARKS
540		0.10	CRYSTALS NOT QUITE SO WELL DEVELOPED BUT MORE COMPL-STAR-LIKE ONES. BALANCE OF GLAZE RATHER STONY
538		0.09	SAME IN EVERY RESPECT AS 536
536		0.08	MOST OF TILE COVERED BY BEAUTIFUL PEARLY CRYSTALS HAS SMALL AREA OF WHITE ENAMEL LIKE GLAZE.
534		0.07	SAME AS 524.
532		0.06	AREA OF CRYSTALS MADE UP OF A MASS OF SMALL FAN-CRYSTALS REST OF GLAZE NICE WHITE MATT.
530		0.05	SAME AS 528.
528		0.04	SMALL AREA OF FAN-CRYSTALS REST OF GLAZE BROKEN BY FEW BUBBLES. HAS NICE MATT TEXTURE.
526		0.03	SAME AS 524.
524		0.02	CRYSTALS APPEAR IN OPEN BUBBLES ONLY. BALANCE OF GLAZE NICE SOFT MATT BUT MANY BUBBLES
522		0.01	SLIGHT SHOWING OF CRYSTALS, BALANCE OF GLAZE MATT.
500		0.00	NO CRYSTALS. SEMI-MATT

small patches of needle crystals can be plainly seen, as well as appearing in the open bubbles.

No. 524.—The trials of this number show about the same difference as in 522, one being somewhat dry and rough, but in a few open bubbles some crystals are to be seen.

The other trial has its surface broken by several large bubbles in which crystals can be noted. The rest of the glaze is a soft matt texture.

No. 526.—In all respects the two trials of this number are the same as 524.

No. 528.—In this set, one trial has developed a small area of crystals, covering about one-quarter of its surface, balance being matt. The other trial does not show any crystals on the surface, but one large open bubble shows a few needles.

No. 530.—One trial has produced a small patch of crystals near the center of the tile equal to about one-fifth of the total area; the surrounding area is matt, while on the edge and end of the tile the glaze is breaking bright, with extremely small crystals projecting out into it from the neighboring matt portion. This seems to point in the direction that the devitrified or matt surfaces are crystalline.

The other tile of this number is a fine soft matt, a few blisters on the border. One open bubble shows a few small crystals.

No. 532.—In this set, one trial has developed crystals over about one-third of its area, large crystals gradually blending out into the surrounding mass of matt glaze. The other trial of this number has a small are of rather fine needle crystals. One open bubble shows crystals on the inside. The balance of the glaze is of a nice soft matt texture.

No. 534.—The best tile of this number has a mass of crystals over about one-half of its area. These crystals seem to grow smaller and smaller from the area of greatest

growth, until they soften out into the sorrounding matt glaze.

The second trial does not show any crystals to the eye, but is a fine soft matt. There still remains one bubble in this glaze.

No. 536.—In this number we get our first strong development of crystals. The tile represented in the cut has become crystalline over its entire surface except for a small part at one corner. In this tile we have the same growth of extremely soft crystals inclosing a small area of the white opaque glaze, similar to 516 spoken of before.

The other tile is a fine matt, a little rough in texture, without any signs of crystals.

No. 538.—Both tiles of this number show a strong growth of crystals, covering all but about one-fifth of the area. The crystals are all pointing to the center of the tile. The outer ring, so to speak, is made up of large fan shaped crystals. These in turn are fringed with a border of very fine silky crystals. This border in turn surrounds a small area of the milky opaque glaze.

No. 540.—While the crystals in this set are not as well developed as in 538, they are well distributed over both trial pieces, forming about one-half the surface. The balance of the glaze is a rough matt, very evidently broken by a crystalline structure.

Conclusions.

In comparing this group with the previous one, it can be seen that the crystalline development in this group is not quite so pronounced as that of Group I. While there are just as good crystals, there are not so many of them.

In Group I we have, in both sets of trials, noticeable crystalline development on twelve tiles, while in Group II we have only ten. This small difference might have been caused by a different rate of cooling at opposite ends of the kiln.

It will be noticed that marked development of crystals begins at about the same point in both groups. At .03 equivalents alumina in Group I and at .04 equivalents in Group II.

It is also quite noticeable that we get our best crystalline development in both groups at about the same alumina content, namely, at 516 and 518, Group I, and at 536 and 538 in Group II, with .08 and .09 alumina content respectively.

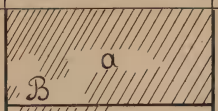
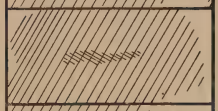
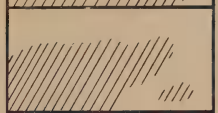
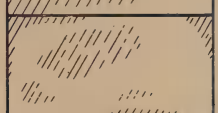
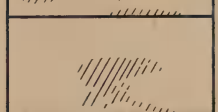
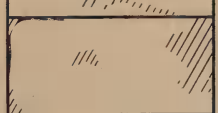
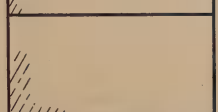
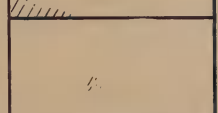
We obtain the same devitrified coatings, badly pit marked by open bubbles, at the low alumina content in each group.

Group III. Alumina derived from feldspar fritted into the glaze.

No. 542.—Both trials of this set are somewhat devitri-

GROUP III.

CONTAINING Al_2O_3 FROM FELDSPAR FRITTED WITH THE BATCH.

NO.		Al_2O_3	REMARKS
560		0.10	TILE IS FRINGED WITH VERY BEAUTIFUL CRYSTALS. SPACE MARKED A IS OPALESCENT, SPACE MARKED B IS A CLEAR GLAZE. END OF TILE MATT.
558		0.09	FINE WELL DEVELOPED CRYSTALS, ALL POINTING TO CENTER OF TILE VERY SMALL AREA OF WHITE ENAMEL.
556		0.08	TILE NEARLY COVERED WITH FINE BEAUTIFUL FAN-CRYSTALS. HAS A SMALL AREA OF OPALESCENCE.
554		0.07	NEARLY THE ENTIRE TILE IS COVERED WITH FINE BEAUTIFUL FAN CRYSTALS. A SMALL AREA IN THE CENTER IS OF A WHITE ENAMEL APPEARANCE
552		0.06	ABOUT HALF OF TILE COVERED BY WELL DEVELOPED FAN-CRYSTALS. REST OF GLAZE RATHER ROUGH.
550		0.05	VERY BEAUTIFUL STAR OR FLOWER-LIKE CRYSTALS, BALANCE OF GLAZE RATHER STONY
548		0.04	LARGE NUMBER OF CRYSTALS JUST APPEARING THROUGH THE MATRIX OF SURROUNDING MATT GLAZE.
546		0.03	SMALL AREA OF LARGER CRYSTALS, SURROUNDING GLAZE SOMEWHAT SOFTER TO THE TOUCH.
544		0.02	A FEW MORE CRYSTALS THAN 542 RADIATING OUT INTO CLEAR GLAZE. BALANCE OF GLAZE DULL AND STONY.
542		0.01	A FEW SMALL CRYSTALS AT ONE CORNER. BALANCE OF GLAZE STONY
500		0.00	JUST A TRACE OF NEEDLE CRYSTALS

fied, with numerous open bubbles. On each trial there appears a small patch of fine needle crystals. The border of each tile shows the glaze to be bright or glossy.

No. 544.—One tile in this set has become rough and devitrified, without any showing of crystals. The other tile still has patches of bright clear glaze in which star crystals have formed. Evidently it is necessary for us to have a fluid matrix for the crystals to grow in.

No. 546.—The trials in this case show a slightly more crystallizing tendency than 544. Both tiles show patches of crystals surrounded by a matt matrix. The latter being blistered quite badly. Some crystals appear in the open bubbles.

No. 548.—One tile of this number is nearly covered with fine bar and star-like crystals intermixed with a devitrified coating, a few bubbles appearing in this coating. The other tile is a soft matt, spoiled in part by a number of bubbles, showing a few very fine bar crystals.

No. 550.—This number has produced very fine crystals on both tile, covering about two-thirds of the surface. There is a marked difference in the crystals on the two trials. In the one case the crystals are of the star or flower type, that is, the bars radiate from a common center in all directions equally. While on the other tile they are only parts of stars shooting forth from the surrounding glaze matrix. Seemingly after these had attained a length of about one-half inch, the ends of the crystals spread out into a fine delicate mass of crystals, so fine in fact that this area becomes almost opaque.

No. 552.—Both tile in this set have formed good areas of crystals, equal to about one-half the surface of one, and about one-third of the other. The tile with the most crystals has a matrix of glaze surrounding the crystals, that is largely crystalline, for they appear very lightly over most of the surface. In the case of the other tile, the surrounding glaze is a nice smooth matt.

No. 554.—At this point the crystals appear in great profusion, overing the entire tile in one case, with crystals

of a beautiful pearly luster. The other tile has well developed crystals over nearly all of its surface, but they are for the most part small needle crystals. At one corner of the tile there is a small area of bright clear glaze into which the needle crystals have spread out like fans.

No. 556.—The crystals in this set have made a strong growth on both tile. They are like beautiful pearl, surrounding a small area of glaze, and have the appearance of opalescence. Very little of the glaze remains in a matt condition.

No. 558.—This pair of trials is very much the same as 556, except that on one tile there has developed an area of

milky opalescence equal to about one-third of the tile, the largest area of this material so far seen.

No. 560.—At this number of the group we still have a fine development of crystals. On the one tile represented by the cut we have a peculiar set of conditions. At one end and side of the tile we have a narrow border of rather dry devitrified glaze, and bordering on this is a beautiful development of crystals, extending almost entirely around the tile. Inside of this band of crystals is an area made up of a clear glaze, and also a fine showing of opalescence. The other tile in this set has developed crystals over about two-thirds of its area, but does not show the variety of glazes or conditions on the one just described.

Conclusions.

This group has produced more well developed crystals than either Group I or II. There is also more uniformity in the two trial pieces of the same number.

A very noticeable feature is the fact that our very best crystals begin to appear at .05 equivalents alumina. The amount that most German formulæ call for.

All things considered, the use of spar as the source of alumina seems to be the most favorable.

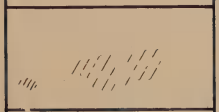
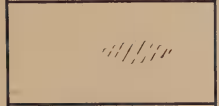
There is less bubbling, smoother glazes and better crystallization. It may be due, in part, to the small amount of K_2O brought in by the spar, acting with the Na_2O and forming a better flux, or in other words a more fluid glaze has been produced, in which the crystals could grow with less resistance. This latter point, in the writer's mind, is very important for the production of well-developed crystals.

Group IV. All alumina used was derived from clay, added in the raw condition to the other ingredients of the glaze, which had previously been fritted.

A very noticeable difference is to be seen in this group when compared with the other three, and that is, that the order of best crystallization has been reversed from the high alumina end to the low alumina end of the series.

GROUP IV.

CONTAINING Al_2O_3 FROM CLAY ADDED RAW TO THE FRIT.

NO.		Al_2O_3	REMARKS
580		0.10	FEW CRYSTALS. GLAZE HARD AND STONY.
578		0.09	FEW MORE CRYSTALS. BALANCE OF GLAZE SAME AS NO.580
576		0.08	NICE SHOWING OF CRYSTALS, REST OF GLAZE STONY.
574		0.07	VERY FEW NEEDLE CRYSTS, GLAZE ROUGH.
572		0.06	LARGER AREA OF FAN CRYSTALS, SURROUNDED BY STONY GLAZE.
570		0.05	VERY FINE FAN CRYSTALS OVER ONE HALF OF TILE, BALANCE STONY.
568		0.04	SAME AS 570
566		0.03	LARGEST NUMBER OF CRYSTALS IN THE GROUP AND THE MOST BEAUTIFUL
564		0.02	NOT SO MANY CRYSTALS AS 566 BUT ARE VERY BEAUTIFUL FAN SHAPED
562		0.01	SOME VERY FINE FAN CRYSTALS SPREADING OUT UNTIL THEY APPEAR LIKE MIST.
561		0.00	A BORDER OF SMALL FAN CRYSTALS EXTENDING OUT INTO A CLEAR AREA OF GLAZE, CAUSED BY A DROP OF SAGGER GLAZE

When this group was first seen it was thought that some error had been made, either in the mixtures or numbering of the group, so an entirely new set was blended and fixed over, the firing conditions being followed as near as possible to that of the previous burn, but there was found to be about one cone difference in the two burns. The first burn reached Cone 10 while the second firing only reached Cone 9 with 10 started. So in writing up this group it has been thought best to compare the trials from the two burns.

No. 561.—This glaze having 1.40 instead of 1.60 equivalents silica has only crystallized as a border or fringe around a small area of clear glaze (caused by a drop of raw lead glaze from the setter). The crystals are rather small, starting as bars and spreading out into fans. The balance of the glaze is a rather dull rough matt.

The trial of the second firing shows a very decided improvement in crystals. Except for a small border on three sides of the tile, the glaze has crystallized completely into numerous bar crystals, crossing and recrossing each other in various directions, producing a very beautiful pearly luster. This trial would indicate that a little less heat than Cone 10 is better for this glaze.

No. 562.—Trial one of this set has developed crystals over about one-half of its area. These crystals seem to have their origin in a rather semi-vitrified coating. The crystals start as bars, gradually dividing or spreading out until they have attained a length of about one-third of an inch, then they shoot out, like the flame to a large gas well, for a half inch more, ending in a rather opaque glaze.

The second trial of this set has become crystalline over about one-half of its area. The crystals in this case are of the bar type, reaching nearly across the tile. The marginal part of the glaze is of a matt nature, soft but breaking rough near the crystal area.

No. 564.—Trial one of this set has an area of crystals equal to about one-third of the tile. The crystals, as in 562, start to grow from the surrounding vitrified coating, and have attained a length of only about one-third of an

inch when they meet other crystals which have grown from one edge of the tile.

In burn two of this glaze about one-half of the tile is crystalline but the crystals, instead of spreading out and forming fan designs, have run aross the surface of the glaze in straight bars. The balance of the glaze is of a dull matt surface.

No. 566.—This trial has attained the best development of crystals in this group. The crystals have grown inward from the margin of the tile to a distance of one-half inch as bar crystals, then spreading out into fan shape, and finally breaking forth into a shape similar to a clover leaf,

having the fine delicate veins or markings of a leaf of that kind.

The second trial of this number has not developed any marked growth of crystals, but the entire central area of the tile is composed of a mass of fine needle crystals, surrounded by a semi-matt glaze.

No. 568.—This glaze has developed an area of fan shaped crystals surrounded by a mass of fine needle crystals, and these in turn by the same semi-matt glaze of the last number.

Trial two of 568 has crystallized over a small area equal to about one-quarter of the tile, as in the other glazes of this group and burn. They have only developed bar-type crystals. The balance of the glaze is of a matt nature by rough.

No. 570.—Trial one of this set shows an area of well-developed crystals equal to about one-fourth o the tile area. The main part of the glaze is a dull matt from which the crystals seem to grow as bars until they spread out into fan shapes. The other trial in this pair is slightly blistered at one end. A small area in the central part of the tile has just a slight showing of crystals which are surrounded by matt glaze.

No. 572.—Both trials in this case show a slight blistering or bubbling. The first burn trial shows a mixture of bar, star and fan shaped crystals, growing out of a mass of fine needle crystals, and these in turn, as in previous glazes, disappear into a semi-matt or matt glaze. The other tile shows a small area of fine needle rystals surrounding a mass of bars, the latter being greatly interwoven. The surrounding matt on this tile is of a somewhat softer texture than its mate.

No. 574.—In the ase of both tiles of this number we find the surface of the glaze broken by numerous bubbles. The glaze is semi-matt, softer in the Cone 9 burn, with no signs of crystals, while the other trial is somewhat rough. It shows a very small area of fine needle crystals.

No. 576.—A small area of bar crystals are to be seen

on both trials, the Cone 10 trial showing the best. Many of the bars have opened into fans. The surrounding glaze in both cases is rough and stony to the touch, and marred by blotches and open bubbles.

No. 578.—Trial one in this set shows a faint trace of needle crystals over a small area, the balance of the glaze being of a dull rough finish, somewhat broken at places by open bubbles. The other trial shows a very nice, fairly soft matt glaze, but around the edges of the tile it is spoiled by small blotches or puffs.

No. 580.—This glaze with the highest amount of alumina added as raw clay in the first burn shows strong traces of fine needle crystals breaking through the surrounding mass of semi-matt. The other burn shows the glaze to be badly defaced by bubbles, some open and others still under the surface.

The main part of the glaze is matt, but at the edges of the tile with a low power glass small needle crystals can be seen.

General Conclusions.

In the groups where the alumina was fritted with the balance of the glaze, spar has proven the best source from which to draw the alumina. As mentioned before, this is no doubt due to the fact that we have a wider range of fluxes present, causing the glaze to become more fluid and hence a better medium for the crystals to grow in.

Aluminum oxide, fritted into the batch, seems to be the next best source from which to obtain the necessary alumina, and, lastly, that of clay fritted as a part of the batch.

The best source found, however, from which to draw the alumina, was that of clay, added raw to the glaze. We have a wider range of glazes from which crystals have developed, but at the same time they are no better than those of the other groups. One other point to be observed is the fact that this group has but very few glazes showing bubbles, while the other groups show large amounts of them.

This phenomenon can no doubt be attributed to the use of gum solution in the first three groups and none in the last.

The addition of .03 equivalents alumina in the form of raw clay was found to be sufficient to cause the glaze to float well, and to adhere firmly to the body. This latter point is possibly the strongest one in favor of the raw clay addition.

It was found next to impossible to apply the other glazes without the use of gum solution.

The most noticeable and perplexing difference in this work is the fact that if we fritt our addition of alumina it causes crystals to develop best from .05 equivalents alumina up to the limit used, namely, 0.1 equivalent, while in the case of Group IV our best crystals begin to appear at the low end, 0.01 equivalents alumina, and continue on up to 0.06 equivalents.

It will be noticed that in both cases they overlap at 0.05 equivalents, tending to show that the formula calling for 0.05 equivalents are about midway in the field, and would be within the field of crystals in either case.

An interesting question is, why has alumina produced these different results—a high amount required in one case and a low amount in the other?

In the writer's mind it could possibly be explained in this way: In the case of Groups I, II and III, where all material in the glaze has been previously fritted, upon burning in the kiln, it melts or becomes fluid quite easy, say at cone 5 or 6, then by the time cone 10 has been reached the glazes low in alumina have become over-fired and devitrified, but the high amounts of alumina have held the glaze from melting early, or have at least prevented devitrification.

Now in the case where alumina was added from raw clay, what conditions have we? We have a mixture that is not as intimate or perfect as in the case of all fritt.

Upon burning this mixture of clay and fritt, what has to take place before we can expect the crystals to develop? Is it not necessary to carry the heat to such a

degree or extend the time to a point where the clay and fritt can reach a state of complete solution?

It is not reasonable to expect to accomplish this as quickly or easily as in the case where this work has previously been done by the fritt furnace.

Now turning to the results obtained in the work, it is only natural that we would expect to see the glazes lowest in alumina mature first. The temperature of cone 10, in a short fire, has only been able to bring the mixture of clay and fritt into a state of combination up to the point where we reach 0.06 equivalents of alumina. Above this amount, while the glazes are nearly vitrified, they are yet in a state of latent fusion, or, just the opposite of the condition of the glazes of Groups I, II and III at the low alumina end.

In conclusion, it may be said that while the use of alumina does not seem to accelerate the growth of crystals, it does act as an agent to arrest the action of the heat on the glazes, giving them a wider range of usefulness. The use of alumina from raw clay is to be recommended, not only on account of its mechanical properties, but because it tends to hold the glazes good over a long firing or a corresponding high fire.

I wish to acknowledge my thanks to Prof. Edward Orton, Jr., to whom I am indebted for the opportunity to carry on this investigation, and I also wish to thank Prof. R. C. Purdy for his valuable suggestions and interest taken in the work.

TESTS OF ASSAY CRUCIBLES, WITH NOTES ON THE TYPES OF CLAYS SUITED TO THEIR MANUFACTURE.

BY

EDWARD ORTON, JR., AND H. B. HENDERSON.

The following investigation is the outgrowth of a commercial commission. Two clays were submitted for the purpose of making crucibles, and instructions were given to find whether either clay, or any mixture of the two clays, would make a good crucible for the assay trade.

This involved a consideration of the work which assay crucibles are called upon to do, a study of how well existing brands of crucibles are able to meet these obligations, and a study of the materials and processes necessary to the production of a crucible which would be able to meet them on their own ground. The work has grown far beyond the scope of the original commission, and has been pursued as an investigation for the interest that attaches to it, and because the subject seems to have been but little considered by others.

The Work of an Assay Crucible.

Assay crucibles are used by the hundreds of thousands annually in all of the great mining districts of the world. The ores of gold, silver and lead are tested by the old fashioned fire assay more often than by any other way. In addition, copper, tin and a number of others are occasionally determined by this method. There are also other fields of usefulness to which crucibles are put, but as a rule the manufacture of crucibles for the ordinary melting of metals, alloys, frits, fluxes, etc., is a separate line from the manufacture of assay goods.

An assay crucible must meet the following requirements:

1. It must be refractory enough to stand the heat of a bright, sharp coke fire, in which it is placed and often times nearly buried. In modern work, the old coke furnaces are largely replaced by single or double muffle furnaces, in which the extremes of temperature vary very much less. A coke fire when freshly replenished is often very cool, and yet by the end of the melt, it may be so white as to make it difficult to see the crucible.

Viewed from the standpoint of a refractory material, the demands made on assay crucibles are not very severe. Any good No. 2 fire clay ought to be able to meet them, so far as resisting the actual fusing action of the fire is concerned. The shortness of the exposure to heat, and the very limited number of fusions to which the ware may be assigned, makes fire failure very rare.

2. It must be able to resist the solvent action of strongly basic fluxes, high in lead and soda, at least to a degree that will permit one, sometimes two and sometimes three fusions to be made without leaking. The corrosion produced on a good crucible should be general and equal all over the slagged surface, rather than local, and should leave the surface smooth, and not pitted and eaten into cavities, in order that the melt may pour out clean, and not leave material adhering in the hollows.

3. It must endure severe temperature changes without cracking, for it is put with its cold charge into the full heat with very little or no preparatory warming, and when the fusion is complete, it is taken out and poured at once and allowed to cool in the open air, when it is recharged and used a second and sometimes a third time. Fusions most commonly go through where the slag begins to burrow into a crack caused by sudden heating or cooling, and very few brands of crucibles will stand more than two severe fusions *with safety* if rapidly heated and cooled, because of failures from this cause.

4. It must be light but hard and strong enough to stand nesting and crating and transportation with insignificant losses from breakage. Often times, in fact very

commonly, they must be transported over bad roads, in wagons or on pack animals, so that transportation is an important element in the cost of the crucible, and heavy breakage would be unusually obnoxious to the purchaser under these circumstances. The clay must have toughness enough to stand the jars and jolts of travel without undue thickness or weight in the walls of the crucible. Extra weight is a very severe limitation.

There are other smaller points which are of influence in the crucible trade, and which help to sell the output—color, shape, freedom from iron pimples, etc., but none of these are of serious influence, if the other points are adequately met.

Development of the Method of Testing.

In the absence of a standard method of testing, or in fact any method of previous work in this line, we undertook to develop a method based on use. As is usual in testing operations, it was the endeavor to make the conditions considerably more severe than those of ordinary service, in order that the resisting powers might be taxed to the utmost, and the wares which were barely good enough might be separated from those which had reserves of strength still left. In developing such a method of testing the following experiments were made:

1. *The Crucibles to be Used.* The Denver 20-gram assay crucible produced by the Denver Fire Clay Co., of Denver, Colo., was used, as these were carried in stock in large quantities in the chemical storeroom of the University for the use of the classes in assaying. They could thus be obtained at wholesale rates, in any quantity, and at a moment's notice.

2. *The Slag.* Assay slags are empirical mixes of strong fluxes which are designed to fuse easily and quickly themselves, and also to dissolve the ore which is mixed with them in the charge. In effect, the assay slag is a fiery solvent, which dissolves the ore into a thin watery silicate, and in that condition applies the reagent needed for the

separation of the metal involved. It parallels exactly the solution of the ore in acids, and the precipitation of the metal from the solution, as is familiar in the ordinary processes of chemical analysis.

The reagents commonly used are litharge or PbO, bicarbonate of soda, carbonate of potash, borax, flint, nitre or saltpetre, argols or crude tartrate of potash, oxide of iron, and a few others. Without going into the theory of fluxing, it may be said that silicious ores are usually given plenty of basic fluxes, basic ores are given plenty of silica or boric acid or both, ores containing lead are dissolved in a reducing slag, using argols to separate the metal and prevent its volatization, while sulphide ores are scorified with slags made oxidizing with nitre to burn out the sulphur.

For the purpose of this test, two very simple slags were proposed

No. 1.		No. 2.	
Litharge	2	Carbonate of potash	4
Bicarbonate of soda	1	Bicarbonate of soda	4
	3	Borax glass	2
		Argols	1
		Ferric oxide	2
			13

Of these, No. 1 was used almost exclusively, as it was found much superior in corrosive power to No. 2. This No. 1 slag was powerfully basic, and capable of dissolving silica from any source at an extremely rapid rate. The idea was to use a slag whose power to attack the clay of the crucible would be at the maximum, and thus observe which crucible could best withstand it. In the preliminary tests, it was found in every case that where No. 1 would not destroy the crucible, No. 2 would not do it, and under conditions where No. 2 failed to destroy the crucible, No. 1 succeeded better.

Determination of the Proper Duration and Proper Temperature for the Corrosion Test.

No exact directions could be found as to the proper

temperature at which assay work should be carried out. Accordingly the following series of tests were made, melting 250 grams of raw slag in each crucible for the length of time indicated, and pouring the slag as clean as possible, and after cooling, weighing the crucible to determine its loss by solution.

The test on following page shows:—

First. There is no important change in rate of solution at Cone 5 (1230°C) over Cone 1 (1150°C). At Cone 1, the slag is fluid enough to pour well, and becomes fully fused in ten minutes, and engages in action on the crucible walls. At Cone 5, there seems little, if any, difference, and certainly no definite advantage. Cone 1 was selected as the temperature for future tests, as it seemed to the eye to be about the same temperature used in the regular practice of assaying, and no advantage had been found by use of the higher temperature.

Second. There seems to be no strongly marked losses in weight from increased periods of solution, above 30 minutes. Below 30 minutes, the losses were lower, but above 30 minutes the losses fluctuate. Therefore, the 30 minute period was adopted for future tests.

Condition of crucibles after test. The records of mere losses of weight by solution of the crucible walls, by a given weight of slag, in a given time, at a given temperature was the fundamental idea of the preceding work. It was early found that the percents loss did not give all the facts necessary to the judgment. The condition of the crucible, the nature of its corrosion, and notes explaining inequalities of corrosion, were necessary from the very first. In the above tests, the first ten crucibles exposed to tests of 30 or more minutes, did not perforate. All showed corrosion less at the bottom, and most deeply from the middle to the top, where the surface of the slag was frothing, and rising and falling. At the bottom, where the fluid slag lay quiet, the surface of the clay was not deeply corroded. Cracks which had been formed in the molding of the crucible, but which were not visible before the test,

Crucible	Weight before Firing (grams)	Weight after Slag Test (grams)	Loss (grams)	Duration of Test (minutes)	Temperature expressed in Cones	Pyrometer Reading in Millivolts	Remarks
1	256.2	243.8	12.4	15.0	Cone 1 or 1150°C	.....	
2	259.6	239.0	20.6	22.5	1150°C	.....	Made in up-
3	255.4	230.5	24.9	30.0	1150°C	.....	draft kiln.
4	257.2	229.3	28.9	37.5	1150°C	.....	Oct. 9, 1907.
5	266.3	241.8	24.5	45.0	1150°C	.....	
6	259.9	231.1	28.8	52.5	1150°C	.....	
7	246.9	266.3	gain 19.4	15.0	.....	.....	
8	258.2	243.2	15.3	22.5	.....	.....	Made in gas
9	247.0	221.6	25.4	30.0	.....	.....	blast furnace,
10	269.5	243.7	25.8	37.5	.....	.....	cone 1 melting in
11	278.3	246.1	32.2	45.0	.....	.....	10 minutes.
							Oct. 10, 1907.
12	258.5	242.5	16.0	15.0	Cone 5 or 1230°C	.....	
13	258.0	245.5	12.5	15.0	1230°C	11.40	Oct. 11, 1907.
14	257.5	237.6	19.9	22.5	1230°C	11.30	
15	265.0	257.3	8.2	22.5	1230°C	11.30	
16	255.1	238.0	17.1	30.0	1230°C	11.40	
17	255.1	258.4	6.7	30.0	1230°C	11.40	Fell over and split slag. Tests no good.
18	256.5	226.9	29.6	37.5	1230°C	11.35	Placed in front 5 minutes, then moved back.
19	245.0	217.2	28.8	37.5	1230°C	11.35	
20	255.0	224.0	31.0	45.0	.....	11.40	
21	259.4	227.0	32.4	45.0	.....	11.40	
22	278.2	255.9	22.3	52.5	.....	11.40	
23	262.7	230.4	28.3	52.5	.....	11.40	
24	259.1	227.8	31.3	30.0	.....	11.40	
25	255.2	227.5	27.7	30.0	.....	11.40	
26	245.1	196.3	48.8	180.0	.....	11.40	*
27	243.2	191.5	51.8	180.0	.....	11.40	*
28	244.1	220.7	23.4	22.5	.....	11.40	

*The contents of these crucibles were still inside at two hours, and were escaped completely in three hours. It is not known at just what time the slag cut through the crucible walls.

were invariably shown to exist by the corrosive eating of the slag. In no case did these cracks let the slag through in 30 minutes. In order to see how long a crucible would stand a continuous exposure to slag, a three hour test was run, but the moment of perforation escaped our attention. It had not perforated in two hours, but had run out and disappeared in three hours.

The failure of the slag to rapidly corrode the sides and bottom of the crucible below the level of the surface of the slag excited attention at once. No adequate explanation can be given for this, but it is a widely observed fact; glass pots, glass tanks, open hearth furnaces, in fact nearly all kinds of furnaces where slags are at work, do their corrosion on the level of the surface of the slag and a little above. Where the slag immerses the surface, the cutting is much slower.

Effects of repeated treatment. In as much as one treatment of 30 minutes was not sufficient to destroy the crucibles, and neither lengthening the periods, nor the use of higher temperatures, seemed to have much effect, the use of repeated treatments was next tried on a batch of six crucibles. The slag from the first fusion was poured off clean, the crucible cooled in the open air, weighed, filled again with a fresh batch of 250 grams of slag, and given a second treatment like the first. The results follow:

TABLE No. 2.

Number of Test	Weight of the Crucible in grams	Weight of Crucible after first heat	Weight of Crucible after 2d Heat	Loss first Heat	Loss 2d Heat	Loss on Total	Pyrometer Reading in Millivolts	Remarks
29	239.9	214.5	178.5	25.4	36.0	61.4	11.00	
30	242.8	218.0	189.0	24.8	29.0	53.8	11.00	Equals
31	256.8	200.9	194.0	25.9	36.9	62.8	11.00	Cone 1
32	244.0	220.2	187.0	23.8	33.2	57.0	11.00	or
33	246.5	225.2	196.2	21.3	29.3	50.3	11.00	1150°C.
34	240.2	223.0	174.2	17.2	48.8	66.0	11.00	

29—Slightly punctured, through bottom.

30—Cut through on cracks in two places. Slag drained out at both.

31—Cut out without crack, high up. No drainage to count.

32—Cut out at a crack. Not much lost by drainage.

33—Cut out at crack, low enough to lose some slag.

34—Sound. Boiled over, but did not perforate.

From the foregoing, it can be seen that the second treatment is more severe than the first, the crucible losing about 10 grams more. Also, only one out of six crucibles endured the second treatment without being perforated by the slag. The cutting out was along cracks in four out of six cases. These cracks may have been formed in the die when the crucible was first made and thus have the title of structural cracks, or they may have been due to the very rapid cooling after pouring the slag the first time, or they may have been due to the sudden heating of the crucible when placed in the furnace. The two latter causes are often powerfully apparent.

There was a considerable amount of boiling over of the slag in these tests. 250 grams seemed only about right in volume, after the slag had settled down, but while active and frothing, there was slobbering in nearly every case. In many cases, the slag which boiled over dissolved out the sand bed from under the crucibles and allowed them to tip over, spoiling the test. To get around this trouble, the amount of the slag was reduced to 150 grams.

Specifications of the standard test. As the result of the foregoing experiments, the following conditions were adopted tentatively as the standard test:

(a) Six crucibles to be used in each test.

(b) 150 grams slag powder (2 parts litharge, 1 part sodium bicarbonate).

(c) 30 minutes exposure in furnace.

(d) Temperature to be that of the melting of Cone 1, or about 1150°, maintained constant by the use of pyrometer.

(e) The slag to be poured out as clean as possible, and the crucible cooled in the open air, weighed, examined, recharged, and given a duplicate treatment.

(f) The standing to be determined, (1) By the proportion of the crucibles that stand the two treatments unperforated. (2) By the relative losses in weight by solution in slag. (3) By the character of the corrosion, i. e., whether smooth and uniform, or pitted and rough.

Application of the Test to Commercial Brands.

In order to establish the grade of excellence or the degree of resistance which the best grades of assay crucibles would offer to the test as above defined, a quantity of crucibles was obtained from all the makers of whom we could get the names in America, and the supply houses were also searched for foreign products in this line. The following is a list of manufacturers whose crucibles were obtained:

1. Denver Fire Clay Co., Denver, Colo.
2. Standard Fire Brick Co., Pueblo, Colo.
3. Utah Fire Clay Co., Salt Lake City, Utah.
4. The Morgan Crucible Co., Battersea, Wales, England.
5. The Beaufay Crucible, France.
6. The Hessian Sand Crucible, Germany.
7. The Dixon Plumbago Crucible, Jersey City, N. J.
8. J. H. Gautier & Co., Jersey City, N. J.

The last four of these brands were not tested in the comparative test, because they were different from the others in shape, size, weight, and thickness of walls, and were thus not capable of a close comparison. The first four varieties were all closely alike in shape, size and weight of walls, and are all extensively used for this purpose in this country. There are a few other makers of crucibles, or makers who have at one time or another made a few and put them on the market, but the number is small and the output is certainly local.

Six of the crucibles of the first four makers in the above list were now put through the slag test as defined

above, in batches, one of each making a batch. Thus, if the furnace conditions were varying, each make got appropriate share of the variation.

TABLE III.

Denver Fire Clay Co.'s 20 gram "Colorado" shape Crucibles.

Number	Weight in grams before firing	Weight in grams after first test	Weight in grams after second slag test	Loss in first test	Loss in second test	Total Loss	Condition after second treatment
1	245.0	235.3	217.5	9.7	17.8	27.5	Sound
2	242.5	229.2	213.5	13.3	15.7	29.0	Perforated
3	245.5	231.8	223.5	13.7	8.3	22.0	Perforated
4	259.0	244.4	221 2	14.6	23.2	37.8	Perforated
5	246.0	232.4	209.5	13.6	22.9	36.5	Cracked, not quite perforated.
6	253.8	242 8	213.9	11.0	28.9	39.9	Cracked, slightly punctured.
Av.	248.3			12.6	19.4	32.1	

Standard Fire Brick Co.'s make from Pueblo, Colorado. Same shape and capacity.

1	246.8	232.2	211.2	14.6	25.0	35.1	Sound
2	247.0	233.2	218.5	13.8	14.7	28.5	Perforated
3	244.6	230.7	205.5	13.9	25.2	39.1	Perforated
4	246.2	232.7	210.5	13.5	22.2	35.7	Perforated
5	234.4	221.4	196.0	13.0	25.4	38.4	Perforated
6	262.8	247.8	221.8	15.0	26.0	41.0	Slightly perforated
Av.	246.9		Ave'ge	13.9	23.1	36.3	

Utah Fire Clay Co.'s make from Salt Lake City, Utah. Same size and shape.

1	250.0	232.5	208.5	17.5	23.8	41.3	Sound.
2	245.0	225.9	200.6	19.1	25.3	44.4	Sound.
3	241.5	233.5	195.7	8.0	37.8	45.8	Sound.
4	251.0	231.8	201.6	19.2	27.2	46.4	Sound.
5	250.5	233.7	206.5	16.8	27.2	44.0	Sound.
6	250.6	231.2	207.6	16.4	26.6	43.0	Sound.
Av	248.1			16.1	27.9	44.1	

Morgan Crucible Co.'s "Battersea" make, 20 grain, "Colorado" shape.

1	285.5	268.5	245.5	17.0	23.0	40.0	Perforated.
2	290.0	263.3	.....	26.7	....	....	Perforated in first trial.
3	279.0	265.5	240.0	13.5	25.5	39.0	Perforated.
4	290.6	276.5	253.7	14.1	22.8	36.9	Perforated.
5	280.7	265.0	237.7	15.7	27.3	43.0	Cracked, not quite perforated.
6	288.7	272.6	244.9	16.1	28.8	44.8	Sound.
Av	285.7			17.2	25.5	40.7	

Using one crucible of each kind and 100 gram Slag No. 2, instead of 150 Slag No. 1.

Denver	258.0	255.6	.....	3.4	Not badly corroded
Standard	246.7	240.7	.....	6.0	
Utah	242.6	235.5	.....	7.1	
Battersea	290.7	286.2	.....	4.5	

In reaching a conclusion on the relative performance of these crucibles, the method described above was as follows:

TABLE IV.

Rank	Name of Crucible	Percentage resisting two treatments without Perforation	Average Quantity of Crucible dissolved in two Treatments	Character of Surface left by the Slag
1	Utah	100	44.1	Smooth and even.
2	Denver	16	32.4	Smooth, even, some cracks & adhering slag.
3	Standard	16	36.3	Smooth and even, some cracks.
4	Battersea	16	40.7	Sand pitted, some cracks.

With this table as a sort of standard or guide as to what the performance of an assay crucible should be when put through this test, the preliminary work was completed, and we were ready to attack the real object of the investigation, viz., the discovery of what types of clays are best suited to this purpose.

Experimental Manufacture of Assay Crucibles from Test Clays.

A number of clays were selected from various sources. A wide variety was purposely employed, in order to discover if possible what influence the composition and physical structure of the clay and its preliminary treatment, might have on its resisting power to the peculiar strains developed in assaying, or by the test we have previously outlined.

The following is a list of the clays and mixtures employed with a description of the peculiarities of each.

(A) This clay was suposed to act as a binder or plastic clay to B, which was supposed to be a promising material for crucible manufacture. When worked up with water is formed a good plastic body with sufficient bonding power and rather tending towards stickiness. It had to be worked rather stiff in order that the crucible would not stick in the die. The drying and burning shrinkage is about 5.5% when burnt to Cone 6. The body is still quite porous and can be easily scratched with steel. It burns to a good buff color, showing numerous iron specks. A partial chemical analysis of a burnt sample shows:

Silica (total)	60.35	of which 24.66 was free sand.
Alumina and Iron Oxide.	37.91	
	98.26	

This analysis indicates a clay containing very few fluxing elements, which its behavior bears out, in part at least.

(B) This clay was a gritty, sandy material of low plasticity. It could only be made into crucibles by tempering it to about the degree used in dry pressed brick or tile. It burns to a good buff color at Cone 6. The body at this temperature is soft and quite porous, easily scratched with steel. Its total shrinkage at Cone 6 is 1.0%. A partial chemical analysis of the clay after burning gave:

Silica (total)	82.49	of which 68.05 was free sand.
Alumina and Iron.....	16.07	
	98.56	

These figures indicate a clay consisting very largely of sand, bound together with a little clayey matter, and such a clay could not be expected to form a dense or reasonably impervious body at any temperature in reasonable reach, or in fact much below its final fusing point.

(C)—Composed of two parts by weight of (A)

and one part of (B). The clays, blended dry by passing through a screen several times, were wet up and made plastic. This mixture worked quite well in the die. The tendency to stick had disappeared and the excessive leanness of (B) had been improved. When burnt to Cone 6, the total shrinkage is about 4.0%. The body is still quite porous, easily scratched with steel, and of a good buff color.

(D)—Composed of one part of (A) and two parts of (B). They were blended by passing through a screen several times. When worked up with water, it developed a little plasticity but not enough to work well. It therefore had to be worked in a condition approaching the dry press process. The total shrinkage at Cone 6 was about 2.0%. The body was quite porous, and could be easily scratched with steel.

(E)—A flint fire clay, from near Canal Dover, Ohio. This is a very hard stony clay, with sharp conchoidal fracture. It has practically no plasticity by itself, and cannot be made into any product without some sort of binding agent. The same vein has been used as the principal ingredient in glass pots, glass tank blocks, and similar refractories for a long period of years at Mineral City, O., a nearby point, and has enjoyed a good reputation for fire brick and common refractories for many years at Canal Dover, Strassburg, Parral, and other points in the northern part of Tuscarawas County, Ohio.

This clay burns to a beautiful light buff color, nearly free from specks of iron, shrinks considerably in firing, and has a good degree of refractoriness, though not the very highest.

The clay was made up into crucibles as follows: The flint clay was run through a jaw crusher and crushed to about a quarter mesh, then put into a ball mill and ground till it would pass a 20 mesh screen. An equal weight of a plastic fire clay occurring in the same deposit with the flint clay was treated in the same manner. The two clays were then blended by passing through a screen several

times. The mass was then wet with water and allowed to stand a day when it worked up into a fairly plastic mass. The clay had to be worked rather dry and required considerable pressure to get a crucible free from cracks. When dry the crucibles were quite tender, but when burnt to Cone 5 they shrank about 5.0% and formed a very porous and sufficiently strong body, easily scratched with steel. A partial analysis of the burnt body showed

Silica	60.01
Alumina	38.89
	98.90

(F)—A plastic No. 2 fire clay from Uhrichsville, O. This is a very plastic buff-burning clay found in large quantities in that vicinity, where for many years it has been used for the manufacture of sewer pipe. It is especially suited for this kind of ware, and the result has been a large output of extra quality.

A selected sample of this clay was made into crucibles as follows:

It was first ground to pass 20 mesh, and a part of this placed in saggers and calcined to Cone 9. Equal parts of the calcined and raw were then blended together. The mixture worked up to a good plastic mass. This worked very easily, and no difficulty was experienced in making crucibles free from cracks and flaws. It dried without cracking to a tough hard body, that could be safely handled. On firing to Cone 1, a very porous highly absorbent yet sufficiently strong body was produced, having a total shrinkage of 2.9%. A partial analysis shows the following:

Silica	66.53
Alumina	33.99
	100.52

(G)—A plastic No. 2 fire clay from Nelsonville, Ohio. This clay is extensively mined at Nelsonville, and has been used in the manufacture of paving brick, sewer pipe and

fire proofing. It vitrifies at Cone 6-8, forming a dense gray body and swells from over firing at Cone 12 or below. It contains a great deal of concretionary iron grains, which form black specks or blisters, according to the temperature attained. It shrinks only moderately in firing, and has a good vitrification range.

The clay was made into crucibles as follows:

A quantity of the clay ground to 20 mesh was calcined in saggers to Cone 9, then mixed with twice its weight of similarly ground raw clay, and passed through a screen several times to insure thorough blending. This was then wet and worked to a good plastic mass and made into crucibles. No difficulty was experienced in working the clay in the crucible die, and a product free from cracks and flaws was easily obtained. The crucibles were dried and burned to Cone 1, producing a strong very-porous, highly-absorbent body having a total shrinkage of 4.4%, and having the approximate composition—

Silica	64.57
Alumina	31.69
	96.26

(L) This batch of crucibles was made from Nelsonville Fire Clay and clean glass sand in the proportion of 20% sand and 80% clay. This clay was ground to pass 20 mesh. The sand was made to pass a 20 mesh, and to lodge on a 40 mesh screen. The clay and sand were mixed and blended thoroughly by passing through a screen several times. The mixture was then wet, and worked to a mass sufficiently plastic for the manufacture of good crucibles, and no difficulty was experienced in producing ware free from defects of manufacture. The crucibles were burnt to Cone 1, producing a porous body of high absorption, and having a total shrinkage of 4.4%. The composition of this body was calculated from the composition of G, and sand (pure silica).

Silica	71.65
Alumina	25.30
	96.95

(H)—A so-called "Pholerite" Clay, from near Versailles, Mo. This clay was selected on the strength of a chemical analysis, which indicated it to be very high in alumina. The clay occurs in rather dense masses; it is easily crushed, breaking with a dull earthy fracture, and when ground in a wet pan develops sufficient plasticity to be easily worked. It has a very high fire shrinkage, and fuses between Cone 34 and 35. Crucibles made from this clay were very free from structural flaws, and exceedingly smooth and talc-like in appearance, but when fired to Cone 9, the total shrinkage was 13.3%, and only a few were obtained free from cracks. The body was dense and the absorption low. The composition was found to be as follows, on a burnt sample:

Silica	51.75
Alumina	45.95
	97.70

(I)—This batch of crucibles was made from the above Pholerite clay, 50% of which was added as grog. The clay was ground to pass 20 mesh, and a quantity placed in saggers and calcined to Cone 12. Equal parts of the raw and calcined material were thoroughly blended. When worked up wet, it developed sufficient plasticity to be worked up into crucibles without difficulty, though they were quite tender when dry. When fired to Cone 9, a very porous and exceedingly absorbent body was produced, yet it was hard and strong enough to meet ordinary requirements. The total shrinkage at Cone 9 was only 1.4%. The composition was the same as H.

(J)—A plastic fire clay from near Versailles, Mo. This is a very pretty No. 2 fire clay, which stands Cone 31, and has good plasticity and bonding power.

A portion of this clay, ground to 20 mesh, was calcined in saggers to Cone 12. A blend was then made, using 50% raw and 50% calcined material. The clay still worked exceedingly well, and would stand a much larger dilution than 50% of non-plastic material. Crucibles free from flaws and cracks were easily produced, and when

burnt to Cone 9, produced a rather dense and very absorbent buff-colored body, having a total shrinkage of 5.1%. The composition of the burnt body was:

Silica	63.95
Alumina	33.63
	97.58

(K)—A plastic No. 2 fire clay, from Crooksville, O. This was an ordinary stoneware pottery clay, which had been washed and filter-pressed. It burns to a beautiful buff body, free from iron specks. It vitrifies hard and water tight at Cone 8 or a little below, but stands about Cone 8 before actually fusing. Used by itself, it shrinks too much and makes a very dense solid crucible. Crucibles were made from the raw clay and fired to Cone 1 with a total shrinkage of 7.1%. The composition of the burnt crucibles showed:

Silica	67.61
Alumina	28.57
	96.18

(O)—A washed plastic firec lay from the Christy Fire Clay Co., St. Louis, Mo. This clay is much used as a bond clay for glass pots and similar high grade refractories. It is a very pretty No. 2 fire clay, with excellent plasticity and bonding power. It fuses at Cone 30 or a little higher. Such clays are in demand in the refractory material trade. A batch of crucibles was made from the raw clay, which worked well, producing an exceedingly smooth and uniform crucible. They were burnt to Cone 4, producing a rather porous body with a fair absorption and a total shrinkage of 13.0%. The analysis of the burnt body shows:

Silica	62.21
Alumina	34.39
	95.60

(M)—The Christy Fire Clay, half raw and half calcined. The dry 20 mesh clay was calcined to Cone 9 in saggers, and blended with an equal weight of raw clay in

the manner previously described. The mixture worked exceedingly well in the crucible die, producing a very uniform crucible, free from defects. When burnt to Cone 4, the body becomes rather dense, but has a high absorption, and a total shrinkage of 4.4%. Its composition has not changed by this treatment, and may be found above.

(N)—The Christy Fire Clay (4) parts, sand (1) part. Clean white sand, that would pass 20 mesh and lodge on 40 mesh, was used. The blend was made in the usual way. The sand did not affect the plasticity to any great extent, but the crucibles were not as smooth and strong as those made with the larger percent of non-plastic introduced as fine grog. When fired to Cone 4, it becomes rather dense, and has a shrinkage of 5.1%. The calculated composition was:

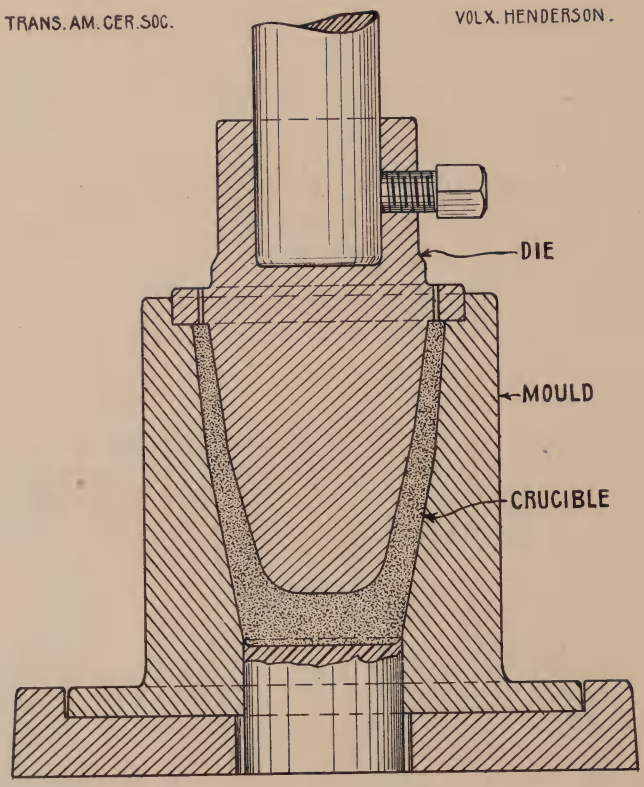
Silica	69.76
Alumina	27.51
	97.27

(1N)—A No. 2 fire clay from Nelsonville, Ohio, as described under G. The crucibles from this clay were made from the raw material only. They were fired to Cone 1, and formed a fairly dense body with a total shrinkage of 6.8%.

Forming of the Crucibles.

The various clays and mixtures were ground, tempered, mixed and prepared as described in the preceding paragraphs (A-1N). When ready, they were molded in a cast iron die, the plunger of which is operated by a screw. Around the circumference and extending through the rim at the top of the plunger, which forms the top of the crucible, is a series of vent holes which permit the excess material to flow out. The circular bottom of the die was moveable, thus permitting the crucible to be forced up and out of the die.

If the clay is too wet, no difference how non-plastic, it has a tendency to stick to the plunger and leave the die.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DIE
MOULD
CRUCIBLE

On account of the air pressure, it cannot be removed without marring and frequent cracking, which renders it worthless. The remedy to be applied in every case is to decrease the tempering water. When tempered just right, the plunger will pull out of the crucible, and it can then be easily forced up out of the die.

There is one defect in crucibles made in this way. The flowing of the clay through the vent holes at the top of the plunger leaves a weak structure at the top of the crucible, and at those places it has a tendency to crack in drying. While the cracks did not go deep enough to affect the results of the test, they mar the appearance of the crucible and would undoubtedly occasion loss in transportation.

Drying. The crucibles, as made, were set on pallets and air dried. No difficulty was experienced in this part of the operation.

Burning. This was done in an updraft test kiln. The crucibles were set by placing one on top of another, top to top, and bottom to bottom. The firing temperature was based on previous tests, or knowledge of the clays' particular properties. The idea was in all cases to keep well below the vitrification temperature of the clays to be fired.

The Test of the Various Experimental Crucibles.

The method of testing was exactly as described in connection with the regular manufactured brands. The following tables contain the details of the test:

TABLE V.

Batch A. Foreign, Plastic or Surface Clay.

No. of Crucible	Original Weight	Weight after First Slag Test	Weight after Second Slag Test	Loss in grams in First Slag Test	Loss in grams in Second Slag Test	Total Loss in Both Tests	Remarks on Condition at End of Test
1	253.3	244.7	237.5	8.6	7.2	15.8	Punctured.
2	256.7	246.5	243.3	10.2	3.2	13.2	Punctured.
3	259.0	249.8	223.7	9.2	26.1	35.3	Good.
4	239.8	236.2	.....	3.6	....	....	
5	244.5	242.7	.....	1.8	....	....	
6	259.6	250.6	223.5	8.4	27.1	35.5	Good.
Av.	252.0	245.1	232.0	5.4	15.9	24.9	

Batch B. Foreign Fire Clay. Very sandy.

1	341.0	333.7	.....	7.3	....	....	All rejected after first test.
2	323.5	313.8	.....	9.7	....	....	
3	329.6	322.4	.....	7.2	....	....	
4	321.5	312.5	.....	9.0	....	....	
5	313.2	305.5	275.6	7.7	29.9	37.6	
6	323.5	314.5	.....	9.3	....	....	
Av.	323.4	317.0	275.6	8.4	29.9	37.6	

Batch C. Two parts foreign clay "A," one part foreign clay "B."

1	279.2	268.0	252.0	11.2	16.0	27.2	Punctured.
2	273.2	260.7	239.3	12.5	21.4	33.9	Punctured.
3	268.1	259.0	233.4	9.1	26.6	35.7	Good.
4	278.3	266.4	245.5	11.9	20.9	32.8	Punctured.
5	264.7	252.5	227.6	12.4	25.7	38.1	Punctured.
6	274.7	260.4	240.8	14.3	19.0	39.0	Punctured.
Av.	272.8	261.1	239.8	11.9	21.6	34.4	

Batch D. One part foreign clay "A," two parts foreign clay "B."

1	296.2	289.8	.....	6.7	....	....	
2	278.1	269.1	.....	9.6	....	....	
3	294.5	285.0	258.3	9.5	26.7	36.8	Punctured.
4	293.2	285.4	.....	7.8	....	....	
5	278.0	266.3	240.5	12.7	25.8	38.5	Punctured.
6	295.8	284.2	258.0	11.6	26.2	37.8	Punctured.
Av.	289.3	279.9	252.3	9.6	26.2	37.7	

Batch E. Flint fire clay one part, plastic bond clay, one part.

No. of Crucible	Original Weight	Weight after First Slag Test	Weight after Second Slag Test	Loss in Grams in First Slag Test	Loss in Grams in Second Slag Test	Total Loss in Both Test	Remarks on Codition at End of Test
1	251.0	245.3	230.6	5.7	14.7	20.1	Punctured.
2	240.0	234.6	228.5	5.4	6.1	11.5	Punctured.
3	247.5	246.1	.....	1.4	....	....	
4	247.7	240.5	.....	7.2	....	....	
5	247.3	242.2	.....	5.1	....	....	
6	238.5	242.0	.....	3.5	....	....	
Av.	245.3	241.8	.....	3.5	10.4		

Batch F. Uhrichsville Sewer Pipe Clay, one part grog, one part raw.

1	261.0	248.3	226.0	12.7	22.3	35.0	Punctured.
2	262.0	251.0	226.6	11.0	24.4	35.4	Punctured.
3	258.5	249.9	225.7	8.6	24.2	32.8	Punctured.
4	272.8	261.5	234.2	11.3	27.3	38.6	Punctured.
5	273.7	262.2	236.7	11.5	25.2	36.7	Punctured.
6	267.2	258.2	231.0	9.0	29.2	38.2	Punctured.
Av.	265.8			10.7	25.4	....	

Batch G. Nelsonville Fire Clay. One part grog, two parts raw.

1	260.3	255.7	223.5	4.6	32.3	36.8	Punctured.
2	257.8	247.3	226.6	10.5	20.7	31.2	Punctured.
3	261.2	254.5	226.5	6.7	28.0	34.7	Punctured.
4	257.8	246.3	221.0	22.5	25.3	36.8	Tipped over 2nd heat.
5	255.9	245.4	218.2	10.3	27.2	37.5	Punctured.
6	258.5	250.5	.....	8.0	....	....	
7	257.8	241.6	218.5	16.2	23.1	39.3	Punctured.
Av.	257.0			11.3	26.1		

Batch H. Pholerite, raw.

1	235.5	275.0	.....	39.5	....	....	All punctured in first heat.
2	235.5	272.0	.....	36.5	....	....	
3	228.2	272.2	.....	44.0	....	....	
4	233.2	293.2	.....	60.0	....	....	
5	238.8	298.0	.....	59.2	....	....	
6	228.3	255.4	.....	27.1	....	....	
Av.	233.2			44.4			

Batch I. Pholerite, one part raw, one part calcined.

No. of Crucible	Original Weight	Weight after First Slag Test	Weight after Second Slag Test	Loss in grams in First Slag Test	Loss in grams in Second Slag Test	Total Loss in Both Tests	Remarks on Condition at End of Test
1	290.5	386.5	.....	96.0	....	....	All punctured in first heat.
2	266.5	354.0	.....	88.5	....	....	
3	301.8	422.0	.....	120.2	....	....	
4	299.7	376.5	.....	76.8	....	....	
5	293.6	410.5	.....	116.9	....	....	
6	278.0	365.0	.....	87.0	....	....	
Av.	288.3			97.6			

Batch J. Plastic Fire Clay from near Versailles, Mo.

1	253.5	239.4	215.2	14.1	24.2	38.3	Good.
2	245.6	233.3	208.2	12.3	25.1	37.4	Punctured.
3	252.7	240.2	212.5	12.5	27.7	40.2	Good.
4	246.4	234.5	206.6	11.9	27.9	39.8	Good.
5	249.7	237.7	210.0	12.0	27.7	39.7	Good.
6	242.7	234.2	205.0	8.5	29.2	37.7	Good.
Av.	248.4			11.9	26.9	38.8	

Batch K. Crooksville Stoneware Clay, raw.

1	251.6	237.8	.....	13.8	....	....	All punctured in first heat.
2	247.8	235.7	.....	12.1	....	....	
3	247.4	234.2	.....	13.2	....	....	
4	244.3	233.6	.....	10.7	....	....	
5	244.7	230.6	.....	14.1	....	....	
6	242.3	226.5	.....	15.8	....	....	
Av.	246.3			13.3			

Batch L. Nelsonville Fire Clay four parts raw, sand one part.

1	319.0	305.5	286.0	13.5	19.5	33.0	Punctured.
2	292.6	277.8	260.6	14.8	17.2	32.0	Punctured.
3	293.2	283.5	256.0	9.7	27.5	37.2	Good.
4	290.2	281.0	257.4	8.2	23.6	31.8	Good.
5	292.2	282.0	257.5	10.2	24.5	34.7	Good.
6	307.6	299.8	.....	7.8	....	....	
Av.	299.1			10.7	22.4	33.7	

Batch M. Christy Fire Clay, one part raw, one part calcined.

No. of Crucible	Original Weight	Weight after First Slag Test	Weight after Second Slag Test	Loss in grams in First Slag Test	Loss in grams in Second Slag Test	Total Loss in Both Tests	Remarks on Conditions at End of Test
1	263.8	256.5	233.5	7.3	23.0	30.3	Good.
2	274.0	271.2	248.5	2.8	22.7	25.5	Good.
3	254.0	245.8	224.0	8.2	21.8	30.0	Good.
4	264.2	255.8	233.2	8.4	22.6	31.0	Good.
5	258.7	253.3	234.3	5.4	19.0	24.4	Good.
6	254.7	247.2	225.7	7.2	21.8	29.0	
Av.	261.5			6.5	21.8	28.3	

Batch N. Christy Fire Clay four parts raw, sand one part.

1	255.4	247.5	.....	7.9	....	....	All failed in first heat.
2	268.1	265.2	.....	2.9	....	....	
3	293.6	290.0	.....	3.6	....	....	
4	259.5	255.0	.....	4.5	....	....	
5	267.0	262.0	.....	5.0	....	....	
6	282.8	281.6	.....	1.2	....	....	
Av.	271.0			4.2			

Batch O. Christy Fire Clay, raw.

1	241.2	236.5	215.5	4.7	21.0	25.7	Punctured.
2	244.5	239.3	216.6	5.8	22.7	28.5	Punctured.
3	236.2	227.5	210.0	8.7	17.5	26.2	Punctured.
4	229.8	223.5	207.7	6.3	15.8	22.1	Punctured.
5	236.0	225.0	205.6	11.0	19.4	30.4	Punctured.
6	239.5	231.2	212.8	8.3	18.4	27.7	Punctured.
Av.	237.8			7.4	19.1	27.2	

Batch IN. Nelsonville Fire Clay, raw.

1	266.7	251.5	228.5	15.2	23.0	38.2	Punctured.
2	267.7	253.2	237.0	14.5	16.0	30.7	Punctured.
3	263.2	248.6	.....	14.6	....	....	
4	278.3	262.0	.....	16.3	....	....	
5	261.8	248.0	223.2	13.8	24.8	38.6	Punctured.
6	264.3	250.5	.....	13.8	....	....	
Av.	267.0			14.7	21.3		

TABLE VI.

Designation of Crucible	Composition of Batch Used in Making	Temperature to which Burnt, in Cones	Physical Properties of Crucibles			Results of Slag Test Averaged from all Trials			
			Absorbtion and Porosity	Shrinkage in percent	Strength	Average Initial Weight in grams	Average Weight Lost in First Test	Av. Weight Lost in Second Test	No. of Crucibles Failing in First Test
A	Foreign Surface Clay ..	6	10.0%	5.5	Poor	252.0	5.4	15.9	2
B	Foreign Sandy clay	6	6.7%	0	Fair	325.4	8.4	29.9	6
C	Two Parts A, 1 part B.	6	12.7%	4	Good	272.8	11.9	21.6	0
D	One part A, 2 parts B..	6	10.0%	2	Good	289.3	9.6	26.2	3
E	Dover Flint 50 per ct. Dover Plastic 50 per ct.	5	12.0%	5.1	Fair	245.3	3.5	10.4	4
F	Uhrichsville S. P. Clay Raw 50, Grog 50 perct.	1	13.6%	2.9	Extra	265.8	10.7	25.4	0
G	Nelsonville F. C. Raw 66⅔, Grog 33⅓ perct.	1	10.0%	4.4	Extra	257.0	11.3	26.1	1
H	Pholerite Raw	9	6.7%	13.3	Fair	233.2	—44.4	....	6
I	Pholerite Raw 50 perct. Grog 50 perct.	9	12.3%	1.4	Good	288.3	—97.6	....	6
J	Mo. Plastic Raw 50, Grog 50 perct.	9	12.3%	5.1	Extra	248.4	11.9	26.9	1
K	Crooksvill Stoneware Clay Raw	1	11.6%	7.1	Extra	246.3	13.3	....	6
L	Nelsonville Clay and and Sand. Raw Clay 80, Sand 20 perct.	1	.....	4.4	Good	299.1	10.7	22.4	1
M	Cristy Fire Clay Raw 50, Grog 50 perct.	4	14.0%	4.4	Extra	261.5	6.5	21.8	0
N	Cristy Fire Clay and Sand. Raw Clay 80, Sand 20 perct	4	.....	5.1	Extra	271.0	4.2	....	6
O	Christy Fire Clay, Raw	4	7.0%	13.0	Extra	237.8	7.4	19.1	0
IN	Nelsonville Clay, Raw	1	10.0%	6.8	Good	267.0	14.7	21.3	3
Utah	.....		13.5%	....	Good	248.1	16.1	27.9	0
Denver	.. ..		11.1%	....	Extra	248.6	12.6	19.4	0
Pueblo	.....		15.3%	....	Good	246.9	13.9	23.1	0
Batters	ea.....		3.0%	....	Extra	285.7	17.2	25.5	1

TABLE VI.

No. Crucibles Failing in Second Test	No. Crucibles Standing the Full Test	Remarks on Cause of Failure
2	2	Loss about equally divided between corrosion and cracking.
	0	Failure due to silicious composition and cracking.
5	1	Corroded deeply, but failure due chiefly to corrosion along cracks.
3	0	Failure due to silicious composition and corrosion along cracks.
2	0	Corroded very deep and made a thick mushy slag that would not pour out clean. Very bad work.
6	0	Loss by deep regular corrosion.
5	0	Corrosion quite uniform with some tendency to corrode in cracks.
	0	Corroded very deep and made a thick mushy slag that would not pour. Tendency to crack.
	0	Corroded very deep and made a thick mushy slag that would not pour.
0	5	Shows slight tendency to corrode in cracks but not bad except in one.
	0	Failure by cracking.
2	3	Deeply corroded by pitting or solution of sand. Very little tendency to corrode in cracks except in the bottom.
0	6	No cracks or deep corrosion.
	0	Deeply pitted by solution of sand. No tendency to crack.
6	0	Strong tendency to corrode in cracks but very slight corrosion elsewhere.
3	0	Failure is due chiefly to corrosion in cracks.
0	6	Deeply but uniformly corroded. No tendency to crack.
5	1	Deep but uniform corrosion. Failure due to corrosion along cracks.
5	1	Deep but uniform corrosion. Failure due to corrosion along cracks.
4	1	Solution of sand grains leaving rough pitted surfaces. Strong tendency to corrode along cracks.

The mass of data presented in these tests is so great that some condensation is necessary in order to comprehend it and grasp the distinctions which exist.

The following table has been prepared for this purpose. For purposes of comparison, the data of the tests of the commercial products obtained on the market is reproduced in the later end of the table:

In addition to the data already tabulated, the following figures on the silica—alumina contents of the crucibles, after firing, is interesting and useful in giving an insight into the causes of failure.

Summary of the results on the Experimental Crucibles.

The data marshalled in the last two tables now begins to show some light on the situation.

We observe:

(1) That clays very high in alumina, i. e., consisting of the purer fire clays, or kaolin-like minerals, offer very poor resistance, when used for assay crucibles. They do not show high losses from solution, but they puncture early, which is the worse evil of the two. The cause of the apparently low losses by solution is not that the clay is not attacked, but that the slag produced is so thick and ropy, and so encumbered with undissolved matter, that it will not pour out well, and leaves much slag adhering to the interior of the crucible. The thickness of this slag is probably due to the excess of alumina set free by the appropriation of the silica by the oxide of lead in the slag. Every clay high in alumina made this kind of slag, and it was not made by any clay not high in alumina.

(2) That clays very high in silica, especially when present in the form of coarse sand, resist the slags very poorly. The sand grains are dissolved out, leaving the structure honeycombed. The clay grains, standing up behind the general level of the surface, produce a very rough, coarsely granular surface. The slags produced are fluid, and pour out well, with no adhering lumps. The crucibles highest in sand were glazed all over the exterior,

with a perfect coating of glass, when the first fusion test was completed, without having boiled over at all. They literally sweated the lead slag through their pore systems, and were entirely unfitted for a second trial, or for use in actual practice for even one operation, on account of the loss of slag through the crucible walls.

TABLE VII.

	Composition of Batch	Chemical Analysis		Behavior of Crucible in Slag Test
		% SiO_2	% Al_2O_3	
A	Foreign Surface Clay.....	60 35	37.91	Slag was slightly thick. Attacked chiefly along cracks.
B	Foreign Sandy Clay.....	82.49	16.07	Thin fluid slag that ran through the body.
C	Two Parts A ..... (Calculated Composition) One Part B	67.72	30.62	Slag sufficiently fluid.
D	One Part A..... (Calculated Composition) Two Parts B.....	75.11	23.35	Thin slag, solution of sand corroded chiefly along cracks.
E	Dover Plastic 1, Dover Flint 1	60.01	38.89	Thick ropy slag, could not be poured.
F	Uhrichsville Raw 1, Grog 1.....	66.53	30.99	Deep irregular corrosion.
G	Nelsonville Raw 2, Grog 1.....	64.57	31.69	Corrosion uniform, fluid slag and tendency to corrode along cracks.
H	Pholerite Raw.....	51.75	45.95	Thick ropy slag that could not be poured.
I	Pholerite Raw 1, Grog 1.....	51 75	45.95	Thick ropy slag that could not be poured.
J	Mo. Plastic Raw 1, Grog 1.....	63.95	33.63	Thin filuid slag, slight tendency to corrode. Only one showed cracks.
K	Crooksville Raw.....	67.61	29.57	Not much solution. Good slag but failed from cracking.
L	Nelsonville 4, Sand 1.....	71.65	25 30	Solution of sand cause of failure. No cracks except in the bottom.
M	Christy Raw 1, Grog 1...	62.21	34.39	Uniform corrosion. Good Slag, no cracks.
N	Christy 4, Sand 1.....	69.76	27.51	Failure due to solution of sand.
O	Christy Raw.....	62.21	34.39	Very slight corrosion except in cracks. Failure due to cracking.
IN	Nelsonville Raw.....	.....	.....	Good slag but failed chiefly from corrosion along cracks.
Utah	.....	75.65	22.13	Good Slag, poured out clean. Deeply corroded, but uniform.
Denver	.....	64.21	33 41	Good slag, deep but uniform corrosion. Failure due to corrosion along cracks.
Pueblo	.....	69.29	28.55	Good slag, deep uniform corrosion. Failure due to corrosion along cracks.
Batters ea	.....	74.97	23.93	Good slag, tendency to corrode along cracks. Failure due to solution of sand.

Mixtures in which a little sand was added to an otherwise good clay, showed these symptoms more or less clearly developed, according to the quantity of sand used.

Clays in which very fine silica was added showed a high rate of loss by solution. The fine grains of silica dissolved like butter, but as they were so fine and so evenly distributed, their solution produced no holes or pits and the surface left after pouring out the slag was smooth and even. The fine flint also seems to have enabled the crucible to stand sudden changes of temperature, both in heating up and cooling down, without cracking.

(3) Vitrifying clays, which made a tight dense body, generally resisted solution in the slag beautifully. But, on placing in the furnace or in removing from the furnace, they cracked in every case, and either in the first or second test, the slag found its way out through the cracks and ruined the crucible. The point of dense vitrification of a clay should, therefore, be well above the temperature of Cone 1, at or below which assays are supposed to be made.

(4) Vitrifying clays, which used by themselves in the raw condition, form a hard dense porcelain-like body, may be opened up and made porous, and able to resist temperature changes, by the use of some chamotte or grog. In our experiments, grog made by calcining the same clay was always used. Where a tight dense-burning clay was thus properly opened up by grog, and fired to just the right point, a body was obtained which resisted solution nearly as well as the raw body alone, and which resisted cooling and reheating very much better. The most successful results were obtained in this way.

(5) A comparison of results of our manufacture with results obtained from commercial varieties tested under exactly the same conditions shows: (M) Christy Fire Clay, one part raw and one part grog, equal to the Utah crucible and better than the other three commercial brands. (C) Composed of two parts (A) and one part (B) is equal to the Denver and Pueblo crucibles, and better than the Battersea, while (F) the Uhrichsville clay,

one part raw and one part grog, and (G) the Nelsonville clay, two parts raw and one part grog, are close competitors to the Battersea.

The theory of crucible body construction seemed from the preceding results to be something like this:

First. Use a clay of neither excessively high silica or excessively high alumina content. In short, use clays of the constitution of the ordinary No. 2 fire clays as they occur in the coal measure formations. A really refractory clay is not wanted and will not give good results, any more than an exceptionally sandy one.

Second. Use grog made from the same clay. Burn it hard, or so near to vitrification that it shall become as nearly insoluble in the molten slag as possible. We have no evidence that grog made from other clays would not answer the purpose, but it would seem the safer course to introduce no new mineral combinations or grains of different coefficient of expansion, when the grog of the same constitution as the plastic clay can be so easily prepared.

Third. The proportion of grog and raw clay to be used, and the fineness of grain of the grog, and the nature and duration of the pugging process, the method of the manufacturing process, and the degree of hardness to which the crucible should be fired before use, are all details to be settled and worked out for each clay. The object to be sought is to produce a body of as dense and solid a structure as possible while still retaining ability to heat up and cool quickly without cracking. Density gained at the expense of power to stand heat without cracking would be worse than useless.

Second Set of Experiments.

In order to put these conceptions to the test, we decided to make up a new batch of crucibles from various clays which we had available, giving each such treatment as we thought most suitable, and then to subject our new product to a competitive test with the commercial brands,

not only by the slag test here developed, but also by actual use by an assayer, on an ore of known value.

The Manufacture of the Test Crucibles.

Six clays of the No. 2 fire clay class, which had given varying kinds of results in the preceding work, were selected, and were made up into crucibles, as follows:

Nelsonville Fireclay, Nelsonville Ohio. (See description in preceding section.) An effort to work in the maximum amount of grog was made, three batches being made. These were marked A, B and I, respectively. A contained 50% grog, but the results were bad and no satisfactory crucible could be gotten. This batch was discarded. B contained 33⅓% grog, prepared as in the first series. I contained 33⅓% grog. The source of this clay was different from B, but both were samples of the Nelsonville fire clay. The process of manufacture was the same as has already been described.

Crooksville Stoneware Clay, Crooksville, Ohio. (See description of clay in preceding section). An effort was made to get 50% of grog into this clay, in order to cut down its tendency to form a hard vitrified body, and therefore one likely to crack, but the attempt failed by the plastic process. The material was too harsh and weak, lacking plastic bond. Success was attained by the semi-dry process, using the clay in little pellets of such a moisture content that they would weld up in the die under the pressure of the screw. This series was marked D.

Uhrichsville Fire Clay, Uhrichsville, Ohio. (See description in the preceding section). No more than 33⅓% grog could be used with this sample, which was taken from the dry pan as it was being prepared for sewer pipe. A series of crucibles was prepared with this composition, and were marked H.

Dover Flint Clay. (See description in the preceding section). This clay consisted of 50% of the No. 2 plastic fire clay used as a bond. No grog was used, as the flint clay operates like grog to all intents and purposes, except

that it shrinks in firing. These crucibles were left over from the preceding work—no new ones were made for the second series. They were enterd only in the assay test and only two were used.

Christy Washed Pot Clay, St. Louis, Mo. (See description in the preceding section). This clay would carry 50% grog and stand manufacture by a plastic process. Its fine bonding power permits this. It was made up in the first series and marked C.

Versailles, Missouri, Plastic Fire Clay. (See description in preceding section). The bonding power of this clay is also exceptional. 50% of grog was successfully carried by ordinary plastic processes. 60% was used by blunging the clay to a cream, incorporating the grog, drying the mixture down to stiff mud consistency and finally molding. The two series were marked F and G respectively.

These various batches, viz., B, C, E, F, and H, together with the Battersea, Pueblo, Utah, and Denver crucibles, were put through the same slag test as described in the earlier part of this paper. The results are as follows:

TABLE VIII.

Composition and Designation of Crucibles	Number of Crucible	First Weight of Crucible	Second Weight of Crucible	Third Weight of of Crucible	Loss in First Fusion	Loss in Second Fusion	Total Loss in Grams in 2 Heats	Condition of Crucible after Test		
								Cracked	Punctured	Sound
Battersea (English) Marked "b"	1	306.5	292.0	.....	14.5	....	....	Crackad	.....	.....
	2	279.5	263.0	233.8	16.5	29.2	45.7	.....	P'nctur'd	.....
	3	292.5	276.0	.....	16.5	....	....	Cracked	.....	.....
	4	286.0	270.0	241.3	16.0	28.7	44.7	"	.....	.....
	5	289.5	275.0	247.6	14.5	27.4	41.9	"	.....	.....
	6	291.5	277.0	.....	14.5	....	....	"	.....	.....
	Av.	290.6					44.1			
Utah Fireclay Company Marked "u"	1	247.0	230.5	201.3	16.5	29.2	45.7	.....	.....	Sound
	2	232.5	215.2	189.5	17.3	25.7	43.0	.....	.....	"
	3	233.0	215.5	186.2	17.5	29.3	46.8	.....	.....	"
	4	232.5	216.0	189.5	16.5	26.5	43.0	.....	.....	"
	5	248.5	232.5	205.0	16.0	27.5	43.5	.....	P'nctur'd	.....
	6	232.5	215.5	192.6	17.0	22.9	39.9	.....	.....	Sound
	Av.	237.1					43.6			
Standard Fire Brick Co. Pueblo, Col. Marked "p"	1	252.0	239.3	211.8	12.7	27.5	40.2	.....	.....	Sound
	2	243.0	228.0	194.0	15.0	34.0	39.0	.....	P'nctur'd	.....
	3	243.5	228.3	202.5	15.2	25.8	41.0	.....	.....	Sound
	4	236.5	223.0	199.5	13.5	23.5	37.0	....	P'nctur'd	.....
	5	253.0	237.0	.....	16.0	....	....	Cracked	.....	.....
	6	253.5	239.0	195.5	14.3	44.5	58.8	.....	P'nctur'd	.....
	Av.	246.8					43.2			
Denver Fireclay Company Denver, Col. Marked "d"	1	289.4	281.0	262.6	8.4	18.4	26.8	.....	P'nctur'd	.....
	2	268.5	247.0	218.0	21.5	29.0	50.5	Cracked	.....	.....
	3	246.0	232.8	206.0	14.2	26.8	41.0	.....	.....	Sound
	4	258.5	244.8	219.0	13.7	25.8	39.5	.....	.....	"
	5	286.5	275.7	252.5	10.8	23.2	34.0	.....	.....	"
	6	256.2	243.8	212.6	12.4	31.2	43.6	Cracked	.....	.....
	Av.	267.5					39.2			

TABLE VIII.

Composition and Designation of Crucibles	Number of Crucible	First Weight of Crucible	Second Weight of Crucible	Third Weight of Crucible	Loss in First Fusion	Loss in Second Fusion	Total Loss in Grams in 2 Heats	Condition of Crucible after Tests: Cracked	Punctured	Sound
Nelsonville Fire-clay ⅔ raw, ⅓ grog. Burnt to Cone 1.	1	289.8	275.0	244.0	14.8	31.0	45.8	Cracked	.....	.....
	2	308.5	290.4	261.0	18.1	29.4	47.5	"	.....	.....
	3	283.3	267.0	245.7	16.3	21.3	37.6	"	.....	.....
	4	267.5	251.5	230.0	16.0	21.5	37.5	"	.....	.....
	5	267.3	249.7	.....	18.6	....	....	"	.....	.....
	6	261.0	245.5	.....	15.5	....	....		.....	.....
	Av.	279.5					42.1			
Christy Fireclay ½ raw, ½ grog. Burnt to Cone 4.	1	257.0	248.0	221.6	9.0	26.4	35.4	.....	.....	Sound
	2	256.8	242.0	214.6	14.8	28.4	43.2	.....	P'nctur'd	.....
	3	245.5	236.5	215.3	9.0	21.2	30.2	.....	"	.....
	4	260.2	250.8	227.5	9.4	23.3	32.7	.....	"	.....
	5	257.2	242.0	220.4	15.2	21.6	36.8	.....	.....	Sound
	6	260.5	248.6	223.3	11.9	25.3	37.2	.....	.....	"
	Av.	256.2					35.9			
Crooksville Stoneware Clay ½ Raw, ½ grog. Burnt to Cone 1.	1	272.2	263.1	.....	9.1	....	....	Cracked	.....	.....
	2	280.0	266.2	.....	13.8	....	....	"	.....	.....
	3	262.5	255.2	.....	7.3	....	....	"	.....	.....
	4	276.0	259.8	.....	17.2	....	....	"	.....	.....
	5	262.0	.....	.....	....	....	....	"	.....	.....
	6	270.3	.....	.....	....	....	....	"	.....	.....
	Av.	270.5								
Versailles, Mo., Plastic Fire-clay, ½ raw, ½ grog. Burnt to Cone 5.	1	272.7	257.0	229.0	15.7	28.0	43.7	Cracked	.....	.....
	2	256.5	240.5	215.5	16.0	25.0	41.0	.....	.....	Sound
	3	263.6	248.8	220.5	14.8	28.3	43.1	Cracked	.....	.....
	4	255.5	243.7	213.5	11.8	30.2	42.0	.....	.....	Sound
	5	269.5	255.8	231.2	13.7	24.6	38.3	Cracked	.....	.....
	6	250.0	232.2	213.7	17.8	18.5	36.3	.....	.....	Sound
	Av.	261.3					40.7			
Uhrichsville Sewer Pipe Clay, ⅔ raw, ⅓ grog. Burnt to Cone 1.	1	258.0	244.0	219.0	14.0	25.0	39.0	Cracked	.....	.....
	2	281.1	265.7	236.0	15.4	29.7	45.1	"	.....	.....
	3	257.8	244.0	214.7	13.8	29.3	43.1	"	.....	.....
	4	281.8	267.0	239.0	14.8	28.0	42.8	"	.....	.....
	5	279.0	266.0	238.6	13.0	27.4	40.4	.....	P'nctur'd	.....
	6	273.8	256.5	229.0	17.3	27.5	44.8	.....	"	.....
	Av	271.9					42.5			

The results of this test are summarized in the following table:

TABLE IX.

Relative Rank	Name of Crucible	Per cent standing 2 tests.	Loss in solution in 2 heats.	Remarks.
1	Utah	83	18.3	One puncture on second heat. General condition: deep, regular corrosion.
2	Christy	50	13.9	Three punctured on second heat. General condition: corrosion deep, uniform.
3	Denver	50	14.7	Two cracked and one punctured on second heat. General condition: corrosion deep along cracks, otherwise uniform.
4	Versailles	50	15.5	Three cracked on second heat. General condition: little corrosion except along cracks.
5	Standard of Pueblo.	50	18.5	Three punctured on second heat General condition is good with somewhat irregular corrosion.
6	Uhrichsville	0	15.5	4 cracked and two punctured on second heat. General condition: deep uniform corrosion.
7	Nelsonville	0	14.6	All cracked. 2 on first heat, 4 on second. General condition: resisted slag well but cracked badly.
8	Battersea	0	15.3	3 cracked first heat, 2 cracked second heat. One punctured second heat. General condition: irregular corrosion, pitting & cracking.
9	Crooksville	0	....	All cracked on first heat. General condition: resists slag well but not the temperature change.

The results here reached do not vary widely from what was developed in the first work. Of the four manufactured brands, the general order is about the same, Utah leading and Battersea being the poorest, while Denver and Pueblo are second and third as before.

The interjection of the test crucibles of our own manufacture brings in some new features however. The Christy comes in next to the head of the column, while the Versailles, Mo., clay is also of the same grade as the Denver and Standard. The Ohio fire clays do not show well, none of them standing two heats, chiefly on account of cracking.

Their solution losses are not excessive, but either the exact method of handling them has not been discovered, or the inherent inability of the clay to withstand severe changes of temperature without cracking is the cause of their failure. Poor as they show in this test, they are about of the Battersea grade.

The Assayer's Test.

Two crucibles each, of twelve different sorts, were furnished to Prof. N. W. Lord, of the Department of Metallurgy of the Ohio State University, with the request that he delegate a competent person to test them. He appointed Mr. P. F. Theobald, E. M., who took the work up and carried it through as shown in his report. The crucibles were all identified by numbers only.

Prof. Edward Orton, Columbus, Ohio.

Dear Sir:—I respectfully submit herewith the following report on tests of assay crucibles:

Twenty-four crucibles were furnished me, and I made the tests of these crucibles using the same method, ore, flux, heat, etc., for all.

All were used repeatedly until they were disabled in some way or other. Most of the crucibles were disabled by cracking, while those that did not crack were eaten through so that they leaked.

The charge used in the crucibles was as follows:

Ore	½ A.T.
Lead Flux	35 gms.
Litharge	20 gms.
Flux Cover	5 gms.
Borax	8 gms.
Nails	3 gms.

The ore used was a silicious gold and silver ore, with about 10% iron pyrites, and a small amount of base.

The lead flux was of the following composition:

$NaHCO_3$	16 parts
K_2CO_3	16 parts
Borax	8 parts
Flour	5 parts

The following table shows the results and behavior of the crucibles throughout the test:

TABLE X.

No. of Crucible	Weight of Gold and Silver Buttons in Grams.													
	Run No. 1	Run No. 2	Run No. 3	Run No. 4	Run No. 5	Run No. 6	Run No. 7	Run No. 8	Run No. 9	Run No. 10	Run No. 11	Run No. 12	Run No. 13	Run No. 14
1	.00295	.00194*												
2	.00292	.00290	.00298*											
3	.00294	.00296	.00270§†											
4	.00294	.00298	.00270§†											
5	.00294	.00298*												
6	.00296*													
7	.00296	.00290	.00182§†											
8	.00294	.00292*												
9	.00296	.00288§†												
10	.00298	.00288†	Froze	.00290§†										
11	.00298	.00292§†												
12	.00296	.00296	.00296§											
13	.00292	.00290§												
14	.00292	.00280§†												
15	.00296	.00292§												
16	.00294	.00290§†												
17	.00292	.00286§†												
18	.00280	.00274†	.00270†	.00274†	.00258†	.00294	.00294	¶						
19	.00296	.00262†	.00282†	.00290†	.00268†¶									
20	.00296	.00278†	.00298	.00298	.00298‡	.00294‡	.00298‡	.00290‡	.00284‡†	.00286‡†	.00296‡	.00286‡†	.00284‡†	.00298§
21	.00298	.00280†	.00298	.00298	.00276‡†	.00272‡†	.00220‡†	.00282‡†¶						
22	.00298	.00298	.00280†	.00296	.00290	.00288‡†	.00292‡	.00288†‡	.00286‡†	.00286‡†	.00286‡†*			
23	.00296	Cupel Cracked	.00298	.00292	.00296	.00258‡†	.00296‡	.00296‡	.00282‡†	.00282‡†	.00282‡†	.00258‡†		
24	.00296	Cupel Cracked	.00296	.00296	.00296	.00276‡†	.00292‡	.00292‡	‡¶					

*=Crucible cracked.
†=Lead stuck; not a clean pour.
‡=Crucible badly eaten.
§=Crucible cracked and eaten.
¶=Crucible eaten through.

The table shows that crucibles Nos. 20 and 23 held out for 14 runs although they were badly eaten after the fifth run.

It is also shown that crucible No. 6 cracked at the end of the first run.

CONCLUSION.

The test shows that the results for all the crucibles check quite closely with one another for the first run. After the first run, most of the results do not check very well, due mostly to the crucibles being eaten and worn, causing ridges and pockets to be formed. The pockets formed were usually first noticed in the bottoms. These pockets usually held some lead and slag, and therefore the crucibles did not pour clean. The lead remaining in the crucibles caused the following results to vary considerably at times, according as the lead stuck or came out with the charge.

Crucibles Nos. 20 and 23 checked very well for the fourteen runs with a few exceptions.

Respectfully submitted,

P. F. THEOBALD, E. M.

The data obtained from this report of Mr. Theobald is of great interest. It shows:

1st. That while most assay crucibles will stand at least two heats, and many will stand more, it is unwise to depend on a crucible which has once been used, for any results of importance. As nearly all assays are of importance and the necessity of exactitude is nowhere greater than in this business, the use of crucibles a second time is always more or less of a risk, and should be confined to duplicate determinations, checking other work, etc.

2nd. It appears from a study of the figures that a prime source of the low figures in second heats is in the pitting and roughness of the surface of the inside of the crucible, and consequent inability to pour the slag out cleanly. This places stress on the maker of assay crucibles

to make them so that they stand the corrosion of the slag with smooth walls rather than pitted and pocketed. This is of much more importance than ability to run many heats, since assayers would not ordinarily be willing to use crucibles more than twice in any case.

3rd. It also places the assayer under stress to secure in every case a fluid, clean slag, which does not stick in the sides or in holes in the crucible in pouring. A thick ropy slag is an almost certain invitation to loss.

4th. On the question of the relation of composition of crucible to resistance to cracking, resistance of solution, and all around effectiveness, the light shed is not very satisfactory.

Bringing the names of the crucibles with the numbers used in the assayer's report, and arranging in order of excellence, so far as can be determined, the following table has been assembled:

TABLE XI.

RANK	NAME AND COMPOSITION	Crucible Numbeas	Heat Run	Total Heats
1	Dover Ohio Clay	23	14	..
	½ flint fireclay, ½ plastic fire clay	24	8	22
2	Utah Fireclay Co	20	14	..
	Commercial	19	5	19
	Denver Fireclay Co	22	11	..
	Commercial	21	8	19
3	Standard Fireclay Co	18	7	..
	Pueblo, commercial	17	2	9
4	Versailles, Mo., Fireclay	10	4	..
	60% grog, 40% plastic	9	2	6
	Christy Fireclay Co	3	3	..
	Versailles, Mo., Fireclay	7	3	..
	50% grog, 50% plastic	8	2	5
5	Uhrichsville, O., fireclay	12	3	..
		11	2	5
	Nelsonville, stock clay	2	3	..
		1	2	5
	Nelsonville, brick clay	13	2	..
		14	2	4
6	Battersea	15	2	..
		16	2	4
7	Crooksville, stoneware clay	5	2	..
		6	1	3

Reviewing here the theories with which the second series was begun (page 35) we find:

First. The theory that excessive alumina or excessive silica in a crucible clay is injurious is not overthrown, for no excessive mixtures were tried in the second series, but it is certainly not strengthened any. The two clays which give the remarkable runs of 14 heats each, and which hold first and second place in the table, are respectively the highest in alumina and highest in silica of the entire list of clays under test.

Second. The doctrine that almost any No. 2 fire clay mixed with hard-burnt grog of its own make, and properly prepared as to proportions, mechanical structure and temperature of firing, will make a good assay crucible, is also neither overthrown nor strengthened. Out of six clays tested, made up into eight different batches of crucibles, only one clay failed to give two good commercial assays. Also, out of twelve batches of crucibles, three commercial brands out of four hold places well to the top of the column for durability under use, while of the eight home-made test batches, only one attained high rank, (the Dover clay, which stood first) while five of them stood at or near the foot.

The Dover clay, which gave the most remarkable performance of 22 heats out of two crucibles, contains no grog whatever. Its flint fire clay component, however, acts like grog, both in drying and after firing. It probably does not act like grog during its first firing process, for the flint clay grains shrink notably, while grog seldom does. After firing, however, the flint clay grains are more or less cracked and shaky from excessive shrinkage, and tend to give the clay body a chance to expand and contract suddenly without cracking, by reason of this very looseneoss of structure. It does not appear, therefore, that the Dover clay is to be regarded as a disproof of the general proposition of the necessity for grog in the crucible clay body.

Third. The proposition that the proportions, treatment, manufacture and burning of the crucible body from

any given No. 2 fire clay, are not matters of rule but of careful study and experiment, and that each clay is a new proposition to be worked out by itself is abundantly supported by the second test.

Fourth. Regarding the merits of the mode of testing devised in the earlier part of this article, and the test of actual use in the hands of a competent assayer, it is interesting to note that the results are about the same from both methods. If the crucibles be given ranks in each, based on the way in which they bore themselves, the data shapes up about as follows:

TABLE XII.

Relative Order	SLAG TEST		ASSAY TEST
	1st Series 6 crucibles of each	2nd Series 6 crucibles of each	2nd Series 2 crucibles of each
1	Christy	Utah	Dover
2	Utah	Christy	Utah
3	Denver	Denver	Denver
4	Standard	Versailles	Standard
5	Versailles	Standard	Versailles
6	Battersea	Uhrichsville	Christy
7	Uhrichsville	Nelsonville	Uhrichsville
8	Nelsonville	Battersea	Nelsonville
9	Dover	Crooksville	Battersea
10	Crooksville		Crooksville

It will be observed that Utah is always first or second, that Denver is always third, that the Standard and Versailles compete for fourth and fifth places throughout. Also that the same five clays bring up the rear in all three comparisons.

CONCLUSION.

The investigation sought to do two things—to find a mode of testing assay crucibles and to determine what type of clay is suited to their manufacture.

Whether the method of test which has been advised here will approve itself to chemists or ceramic engineers after further trial and use is an open question. It cer-

tainly seems to offer a fairly simple and workable plan. Its results seem, in this instance at least, to coincide fairly well with such classification as actual use would give. To be sure, the conclusions here drawn depend on too little evidence, and too few trials to be regarded as more than tentative, but until better ones are available, they are entitled to consideration.

On the second point, the conclusion is reached that clays suited for making assay crucibles are rather common and easy to find. They need not be extremely refractory, nor can they be very easily fusible. They should not be excessively silicious, nor excessively aluminous. They must be worked with plenty of grog or equivalent, in order to stand sudden and severe changes of temperature. The details of their manufacture is a special problem to be worked out for each clay. What the exact quality or combination of qualities is, which makes one clay superior for this purpose to another, has not yet been established. There is no method yet known how to tell a crucible clay except to make crucibles of it and prove their quality.

DISCUSSION OF THE RECOMMENDATIONS OF THE SOCIETY'S COMMITTEE ON CO-OPERATION—ESPECIALLY THEIR RECOMMENDATIONS TO THE STATE GEOLOGISTS.

PROPOSED BY

HEINRICH RIES, Ithaca, N. Y.

In proposing this subject for discussion before the society, it was not done with the intention of advancing any personal views on the matter, but rather with the object of obtaining an expression of opinion from members of the society outside of the committee, and the fact that the report has been published in sufficient time for members to have read and digested it, makes this possible.

The subject is an exceedingly important one, and in view of the fact that the committee was not unanimous on all points, I believe it all the more desirable to see what the general opinion of others is on the several points involved in the report.

Some state geologists appear to be rather alarmed over the long series of tests proposed, and have inquired whether it is necessary to go through all of them in order to find out what a clay is good for. Many ask whether the committee cannot recommend some preliminary tests, which will enable them to determine without much trouble whether a clay is worth further testing.

A second disturbing fact is the apparent cost and size of the equipment necessary in order to test the clays.

I think all of us, however, are agreed that survey reports dealing with clay should be as complete as possible, in order to make them of value to the practical man, and the question which to my mind may be debatable is, whether the committee report places proper emphasis on all the points considered, and whether it has omitted any essential details.

Among the points included in the state recommendations, on which it seems to me there is cause for discussion, are the questions of burning and chemical analysis. With regard to the former, one may question whether the construction of a curve such as that suggested, will be of much value to the average clay worker, interesting as it might perhaps appear to a trained ceramist. Its development, however, calls for no burning test above Cone 11, while that is by no means the highest heat reached in the ceramic industry. Should not the recommendations, therefore, call for a burning test at higher temperature? In the case of refractory clays, a high temperature test is called for by most practical men, and although the curve above refererd to is said to enable us to class a clay as refractory, it does not tell us what its fusion point is.

It will also be of interest to get the views of the society at large regarding the value of a chemical analysis. If it is of value only in certain cases, would it not have been well to mention these?

I do not doubt that there may be other points which may be suggested by others, and I hope the society will discuss the matter in full.

NOTE ON THE RECOMMENDATIONS OF THE COMMITTEE ON CO-OPERATION WITH STATE GEOLOGISTS.

BY

S. Geijsbeek, Seattle, Wash.

The recommendations as submitted are very good to a great extent. They have, however, some defects to which I wish to call attention.

They recommend that these Surveys go to a very large amount of work in order to test a clay, without any assurance whatever that these tests will be of value as far as the tested clay is concerned. It would have been far better to recommend first a fire test to determine whether it be advisable and deemed economically of value to go to the prescribed tests in order to get at the different properties of the clays. If Surveys go to all the trouble and expense to test clays, according to our recommendations, and then find that only about 75% of the clays tested have any value for clayworkers, they will throw cold water on our recommendations.

Under the heading "Properties of Clay," I do not find that the tensile strength test has been recommended. This test has certainly a great value in the determination of the physical properties of clays, as it is a good indication as to the bonding power of such clays.

Another point in which the recommendations are totally lacking is the tests in regard to the refractoriness of clays. One of the first questions one is asked in regard to the testing of clays is how high a heat will it stand. The committee only recommends vitrification tests to Cone 11, a temperature sufficient for low grade clays, but which will give us no indication whatever as to the refractoriness of high-grade clays.

A fusion test is, in my opinion, just as essential as a

vitrification test, and should be incorporated in the recommendations.

The condemnation of the laboratory test kiln is a step in the right direction, and if carried out, will help greatly in the determination of the value of clays. I hardly think there has been enough provision made regarding the chemical analysis. While we all know that the chemical analysis will not give us enough data to judge the value of clays, it will give us a strong point in determining some features which could not be otherwise determined. The total absence of the mentioning of the rational analysis is another defect in the work of the committee.

NOTE ON REPORT OF COMMITTEE ON CO-OPERATION WITH GEOLOGICAL SURVEY.

BY

R. R. Hice, Beaver, Pa.

Personally I am glad that Dr. Ries has placed this subject for discussion before the Society. Since the report of the committee was made I have talked and corresponded with a number of State Geologists who are interested in this subject, and one of the inquiries relative thereto was in reference to the matter of field analysis, which in some states, at least, would be most valuable, if such a scheme can be devised.

In some of the states we find all kinds of clays—fire clay, plastic and non-plastic, sedimentary and residual clays, fossil clays of past geological ages and clays of recent deposition, shales and glacial clays of infinite variety, etc.—while in other sections of the country we have clays that are suitable for nothing but the most common products. For these reasons the State Geologists do not have in all cases the same problems, and for the same reasons portions of any scheme of testing will not be applicable in every region. The tests must therefore embrace much that would be unnecessary in some sections, and, in the absence of such information as is suggested in the recommendations to the U. S. Geologists, any general scheme will undoubtedly omit some tests which should be applied, to higher grade clays especially. At the same time it must be expected that the State Geologist will very properly raise the question whether or no he should point out the special adaptability of any particular clay to the production of any special product. The question raised by Dr. Lane, of the possibility of field tests which would eliminate much useless material from further study, seems

to me most valuable from the view of the geologist, and it is certainly of no advantage to the ceramist to have a lot of useless work done in the laboratory. Dr. Lane has had a detailed study of the waters of Michigan under way, and the field analysis of water has rendered possible such detailed work. Few of us, perhaps, appreciate the peculiar advantage of a small pocket case, filed with reagents in tablet form, over the ordinary laboratory water analysis; but the tablet has not rendered laboratory work unnecessary. The entire state of Michigan is covered with glacial deposits with a vast number of glacial clays, most of which are calcareous. Many of these are absolutely useless, yet in the field one cannot determine the fact.

Dr Lane asks, "Cannot a test be devised that will at once show the *uselessness* of some of these clays?" It certainly seems that something might be done in this line. A small portable furnace might be valuable as part of such equipment.

In the recommendations made to the State Geologists chemical analysis was purposely omitted. None of us really place much value in analyses as they are now made. I had a case of this kind before me recently. A clay had been analyzed and the report started out with the statement "no soluble salts present." Then followed the tabulated result of the work showing CaO and MgO present, closing with a percentage of SO_3. Now I do not imagine that SO_3 was lying around loose in the clay in an uncombined state in the presence of lime and magnesia, nor do I think if combined with lime or magnesia there were no soluble salts present. As now made, a chemical analysis makes practically no attempt to show the various chemical compounds present, and until we have this knowledge and the amounts of these compounds, which are the constituents of a clay, we cannot expect any real advantage from chemical analysis, and only when we have the knowledge of the compounds present can we make a proper rational analysis. In this we are in the same position as the student of fuels. Ultimate

analyses of fuels have been made in countless numbers, but their value is relatively small, and today the demand is not for the percentage of C, O, H, etc., but the proportions of the various hydro-carbon compounds present. I fully believe the proper study of the technics of clay analysis will result in such improved and changed methods as will give the desired information.

Another test omitted in the State recommendations was the tensile strength test. The value of this test seems to me very doubtful. When made on a clay it shows the combined effect of several properties; cohesion, adhesion, etc., which are affected by the size and also by the shape of the clay particles, and consequently the result of a tensile strength test cannot be used as a factor for any other sized particles of the clay, nor as a factor representing the bonding power of the clay when grog of any kind, size, or shape is used.

The fact that most clays coming to the view of the State Geologist are of low grade must not be overlooked. I must agree with Prof. Binns that it is rarely we need to go beyond Cone 10. By far the greater number of clays will fail at a low heat. Again it is the object of the Geological Survey, I take it, to only point out such facts as show the inherent qualities of clays, leaving the manufacturer to determine the use for any specific purpose.

We at present have very little real knowledge of clay, and it must be said that we are confronted with the practical proposition that the present unsatisfactory state of the knowledge of clays is due largely to the want of harmony among clay workers. Nothing is more needed than a determination of the proper tests to apply to clay. Old as the industry is, and as diversified as it has become, we must all agree that we have practically no real knowledge. We are in the same position as the iron industry was not many years ago, but it has advanced with vast strides, while in ceramics we are still in hailing distance of our position of many years ago. Our knowledge of higher class goods is rapidly increasing, but regarding the foun-

dation, the clays themselves, we have been at a stand still. This is not as it ought to be. Standing so near the top of the manufacturing industries, it is not right that we should be compelled to admit that we hardly know what a product will be until it is out of the kiln. Yet such is the case, and no real progress will be made until the clay people get together in some harmonious manner. If the clay industries put up the demand for the critical study of the subject its importance demands, and are a unit in demanding of Congress that a proper appropriation be made, of a similar magnitude to that made for the fuel tests, then we may expect results, and the questions daily arising can be solved; but, in the absence of a united front toward Congress, we can only look for such work on behalf of the United States as is required to meet the demands of the several departments, and these are largely met by testing the finished products for strength,—and not such studies as point out the defects of methods of manufacture or faults inherent in the materials used, or how these may me met and corrected. A start by the U. S. Survey in testing of clay goods will be made this year, but the present views of Congress, as expressed in the limitations of the appropriation bills, are not to encourage any real study, but these conditions could be easily met if the clay workers would hold together.

DISCUSSION.

(None of the authors of the preceding "Notes" were present at the meeting. Prof. Parmelee read the communication from Dr. Ries, and Prof. Orton read that from Mr. Geijsbeek and stated that he had received from Mr. Hice, then in Florida, a letter in regard to the inquiry of Dr. Lane upon the question of how far field tests can be used in determining the value of clay. The note from Mr. Hice, printed above, has been sent in since the meeting.

It has been necessary, on account of the limit placed upon the number of pages in this volume, to abridge con-

siderably the discussion that followed the presentation of this subject.—The Editor.)

Mr. Orton: There is, in the last part of the program, the title of a note by Mr. Hice, "How far can Field Tests be used in Determining the Value of Clays?" I request your indulgence, if I bring the discussion of this question in at this time. This question really is by Dr. Lane, State Geologist of Michigan. It is one of the first fruits of our co-operation committee's work. He has brought in a practical query from the standpoint of a man who has work to do. He wants light. Dr. Lane's problem is about the same as those indicated by Mr. Geijsbeek and I think by Dr. Ries, viz., how much of this work of testing clay samples should be done on samples of which we know nothing? How far does it pay us to make these long investigations, when, as Mr. Geijsbeek puts it, seventy-five percent are "no good" when tested?

Dr. Lane evidently has run into this practical problem because they have in his state, he says, a large percentage of drift clays whose value is limited to soft mud common brick and drain tile. He says, "Must my men go into the field, sample these clays, send large quantities of them to the survey station, and put them through the formal test recommended by your committee to determine their value? Can we not have a "field test" on the sample, made either in the field or at the village or hamlet at which the sampling expert will stay the next night? May we not by some such a test, have sufficient warrant to send them in to the station for further investigation, or to reject them altogether?

Mr. Hice wrote me that in his opinion it would be a simple matter to devise a rough apparatus by which the content of free carbonate of lime in a clay could be determined in the field, and information obtained which would throw the clay out at once, or entitle it to fuller and better test.

Mr. Hice also propounds the question as to what the members of the society may think of a portable gaso-

lene muffle-furnace in which short tests could be made, setting it up anywhere, and getting results in two or three hours sufficient to warant throwing a sample out, or carrying the investigation further.

Mr. Stover: If any way can be devised of doing the preliminary work within say twenty-four hours, as suggested, so we can tell whether the clay has any commercial value at all, it seems to me it would be a very important point for the state surveys to have that information. But, assuming that you have reached the conclusion that you have a highly refractory clay that will make a fire brick, do the members believe that Cone 11 will be a high enough fire for a clay which has gone through the preliminary test and tested out as a fire clay? I do not believe it is high enough. So I will ask, as much for information as anything else, why not in cases where it is assumed that you have a highly refractory clay accept the German Standard and fire, say, up to Cone 27, and give a full report? In any case, when the first test has been devised, I can see no reason why both the chemical and rational analyses should not be given.

Mr. Fox: I had occasion in Illinois to test quite a number of clays sent in from different parts of the state for the State Geological Survey. As was said by Mr. Geijsbeek, about seventy-five percent of these clays sent in are exceedingly poor grade. So far as a test for the calcarious clays is concerned, I think it will depend largely upon circumstances. Sometimes in the field we find lime in lumps large enough and in quantity enough to condemn the clay at once. On the other hand we have had clays sent in that, so far as an examination would show, nothing could be told about the value of the clay for the manufacture of ware, so far as the lime content was concerned.

The question as to whether or not we can readily test clays which may be more refractory, I may say the indication process is quite simple. We used for these preliminary tests an ordinary gas kiln, gas and compressed air. The samples were made up in the form of Seger cones

and were mounted on placques with the standard Seger cones, distributed in such a way that when the clay failed, the cone at which it failed would also be indicated. I found with a small furnace it was possible to carry the burning test in not more than six or eight hours up as high as Cone 30. For our common shale clays, we can begin, say with our placque set with Cones 1 to 10, and our second burn carrying us from ten usually to the failing point of the clay; and with our small furnace the heat can be raised rapidly so the tests can be completed in from two to eight hours, depending on whether two or more burns are necessary.

Mr. Binns: I have had this matter under some consideration, and I have read the report somewhat carefully; and I think upon the whole I agree with the view that some further recommendations be made, as suggested by Dr. Ries and Mr. Geijsbeek. It is only rarely that we want to go beyond Cone 10. Refractory clays are not so abundant as they might be. It is true that probably ninety percent of the clays can be condemned or partially approved with a very simple test.

Now, as to the possibility or practicability of a field test which will be available in the hands of the field man, I rather fear that unless he were an especially trained clay man, there would be some difficulty; because we all know how very high in the examination of clays the personal equation is. Those who are always handling clays can come to more reliable conclusions than those who approach the question from a geological standpoint, and the geologist who does the ordinary field work is not an especially trained clay man. I do not know whether they are putting specially trained clay men in the field, or giving the work to those who are undertaking geological studies simply.

I think the idea of a portable gasolene furnace is probably better and more satisfactory than a portable quantitative analytical outfit. The recommendation of the gasolene furnace, at the same time, does not chime with the committee's recommendation as to the abandonment of the

common laboratory kiln. And if the laboratory kiln is condemned for its work, can we devise a gasolene furnace which will give better results in the field than this does in the laboratory? I should like to see burning tests carried out tentatively in the field, but I do not see how we can expect to arrive at satisfactory results by the use of a very small furnace in the field, or results different from those which have led to the condemnation of the common laboratory kiln. It has been rather interesting, as showing the difference of opinion or the uncertain state of opinion on this subject, to hear objections raised, on the one hand, that state geologists are being put to too great expense; and, on the other hand, the suggestion that tests should be carried higher than Cone 11. The suggestions to the National Government are admirable, I think, on the whole; but in regard to the suggestions to state geologists I think we will rather scare them into doing no work by the fact that the specifications laid down are so heavy that few will feel able to undertake work of that character and scope.

Mr. Moore: I believe that the porosity and specific gravity determination, as determined on pieces burned at different temperatures, furnishes the best means of judging the commercial possibilities of a clay.

In regard to the gasolene kiln for high temperature work, I would say that I do not believe it is reliable enough to base a scientific opinion as to the refractoriness of a clay. My reason for this is that the gas flame striking the cone causes it to bend at a temperature far below its correct melting point. Such a kiln should, I believe, be used only in preliminary work.

Mr. Yates: I think the analyses of the clays should be the clay worker's guide. The analysis is what the practical clay worker goes by. The next test is the burning in the kiln. I would like to know if a man can get satisfactory results by this testing? A man puts a piece of crude clay in a furnace and burns it and gives his opinion, but I would not think much of that test. What we

want is the analysis. If it is worth doing, it is worth doing well.

Mr. Fox: I think the gentleman who just spoke is under some misapprehension as to the method of sampling the clays to be tested.

I agree with the proposition that anything worth doing is worth doing well,—yet I have yet to be convinced that the chemical analysis of a clay will tell even the practical clay man very much of the qualities of the clay. I claim in some respects to be a practical clay worker myself; but if I were going to rely on any one thing it would be upon the pyrometric test of the clay, rather than upon the chemical or physical conditions of the materials, because there are so many things in the clay mass that we cannot possibly get at in any other way than by a pyrometric test.

The use of a small kiln, which seems to be the point under discussion, is not for the final determination, but simply for weeding out the materials that are useless; and when it comes to the examination of the small number which will pass the test of the small kiln, then it is worth while to go into the more elaborate tests.

I am inclined to think it would be better to have the samples sent to the laboratory rather than try to make these tests in the field. Any survey which goes far enough to send a man into the field to collect samples will certainly not object to paying the small amount required for expressage to send the samples to the laboratory, where they could be much more satisfactorily treated.

Mr. Purdy: If we omitted high temperature tests for fire clays, it was a mistake. The fact remains, however, that all clays which stand Cone 26 are not refractory in sense of being a No. 1 fire clay and serviceable in wares requiring open structures. In our tests Cone 11 happened to be the maximum cone to which vitrification rate was tested. It was not intended that the test be limited to Cone 11.

As to the chemical analysis, what I said as to the

refractoriness of clay will also apply to the chemical analysis. We cannot tell much from the ultimate chemical analysis, for instance, as to suitability for paving brick manufacture.

PORCELAIN FOR ELECTRICAL PURPOSES.

A REPLY TO THE DISCUSSION OF THIS PAPER, BY EDWARD ORTON, JR , IN VOL. IX.

BY

A. S. WATTS.

In Volume IX of the Transactions of this Society, there appeared under the head of Discussion, in my article on "Porcelain for Electrical Purposes," an article or criticism from the pen of Professor Orton, to which I wish to make reply.

(1) Professor Orton says in his opening statement: "Mr. Watts has perhaps shown that discretion is the better part of valor in not attempting to deduce conclusions from the foregoing evidence, for there is much that is contradictory in his figures even when correlated and reduced to their lowest terms." In rebuttal, I call attention to page 608, on which I state specifically that the table offered compares maturing temperatures with dielectric strength, and these are compared and a statement made in the lines immediately following. The above remark was obviously unjust, for I did draw a direct conclusion from the data offered.

Further, the second part of my article, which was the portion calling forth Professor Orton's discussion, was a note added as an afterthought and was not offered as conclusive evidence, but merely as additional evidence to show that the dielectric strength of porcelain increased as vitrification increased, even past the point where warping develops to a pronounced degree, thus justifying the statement elsewhere set down, that we cannot expect maximum tensile and abrasive strength and maximum dielectric strength in the same porcelain. This fact is not only shown in the data offered, but the conclusion is stated in so many

words on page 608; hence, the statement that I did not draw conclusions is erroneous. In fact, Professor Orton, after studying the data offered, on page 615, reaches a conclusion which is almost identically the same as my statement made on page 608.

(2) He next states that "A part of this difficulty comes from the structure of the series itself, in which there are too many variables."

This statement is also misleading. Professor Orton has never, so far as I know, constructed a series in which there were as few variables as in this series. He always taught in his class work to form series by substitution, which necessarily introduces two variables. In the series presented in my table, the porcelains run from 0.15 RO, Al_2O_3, 5.5 SiO_2 to 0.50 RO, Al_2O_3, 5.5 SiO_2, in which only the RO varies. Further, it is plainly apparent, that the whole variation is in K_2O alone, which runs from zero up to 0.35, and in equal steps of 0.025 equivalent each. Can a series be made with less variables than this? Does the fact that I have chosen to vary by *additions to* a formula, instead of by *substitution in* a formula, make my work fairly open to Professor Orton's charge of too many variables?

(3) He next says that one end of the series "is fluxed with lime alone, and would not be seriously expected to produce desirable results." It seemed to me advisable to extend this end of the series to zero K_2O, since in the formation of the series with .15 CaO constant, this was one of the natural extremes. In fact, it is almost invariable in the forming of a series of ceramic mixtures to discover the effect of one or other of the ingredients, to carry the extremes well beyond the point of favorable results. How else can the area of permissible variations be known, except by pushing the variations beyond the permissible and by the very failures produced, show that the boundary has been passed?

(4) "On top of this comes the consideration of the behavior of these bodies at three different temperatures."

says Professor Orton. On page 608, in introducing the data, I stated that I was offering a table in which the dielectric strengths were comparable with the maturing temperatures. To do this it was necessary to cover the range of temperatures between Cone 6 and 12, and I said in explanation that the same phenomena were observed in this set of trials as were noted in the former paper on this subject, etc. Was this firing at three different temperatures an error, which, as Professor Orton implies, makes the paper less valuable or more difficult to understand? Rather, does it not furnish exactly the data intended; i. e., enable us to compare the dielectric strength with the maturing temperatures?

(5) Lastly, Professor Orton rather condemns me for not going further into the interpretation of the data offered, and proceeds to endeavor to interpret it for me. However, he ends up (as I could have warned him he would) by stating that "flaws are so hard to detect and are such a fruitful source of error that only by resorting to an average of a number of tests can we learn anything reliable as to tendencies." This last statement is correct, and it is a justification of my course in not attempting to deduce conclusions of importance in the case, for the very reason that he gives, viz., there was not a sufficient number of tests to give us the necessary averages for reliable conclusions.

PORCELAIN FOR PRACTICAL PURPOSES.

Further Discussion by EDWARD ORTON, JR.

Replying to Mr. Watts' second note on this subject in which he takes exception to some of the points of my first discussion, I may say that in item (1) Mr. Watts undoubtedly has the best of the argument. On page 608, he does announce the purpose of forming the series on page 609, and immediately after, does in an informay way announce that the results made good their purpose. I was mislead by his last sentence, on page 611, in which he says "Any attempt to discuss the foregoing would make too lengthy an article, and I, therefore, have decided to offer the data and leave the interpretation to you." From this sentence, I naturally concluded that Mr. Watts did not himself think he had deduced conclusions from his data, and did not hunt back in the earlier portions of his article to find them. An effort to interpret the data seems to be partially invited by Mr. Watts' own words, and their publication without interpretation either by the author or someone else, seemed at the time and still seems to me to be scarcely worth while.

(2) On the question of the method of forming series, whether by substitution or addition, much may be said. Mr. Watts is right in criticising my statement of the *number* of variables. My statement was loosely made and is not technically exact as all statements ought to be, especially when made in criticism of another's views. But, while technically inexact, I still think that I was right in the broader sense—for his *additions* have produced a series of such very wide range of properties, that it has to all intents and purposes made close comparison impossible, and that was what my statement meant. I should have said "in which there is too wide a variation" instead of "too many variables."

On this question of series by substitution vs. series by addition, it may be said that the former does necessarily involve two variable members, but a body or glaze of more or less practical type is assured at all points between the extremes, if the latter are well designed.

Take for instance Series I of porcelains:

	(1)	0.35	K_2O	0.15	CaO	1.00	Al_2O_3	5.50 SiO_2
	(2)	0.30	K_2O	0.20	CaO	1.00	Al_2O_3	5.50 SiO_2
Series I	(3)	0.25	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2
	(4)	0.20	K_2O	0.30	CaO	1.00	Al_2O_3	5.50 SiO_2
	(5)	0.15	K_2O	0.35	CaO	1.00	Al_2O_3	5.50 SiO_2

in which substitution is practical between K_2O and CaO, versus Series II:

	(1)	0.35	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2
	(2)	0.30	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2
Series II	(3)	0.25	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2
	(4)	0.20	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2
	(5)	0.15	K_2O	0.25	CaO	1.00	Al_2O_3	5.50 SiO_2

in which the changes are by *subtraction from* and not *substitution in* the formula.

The equivalents of the four materials from which these two series of bodies would be compounded, are as follows:

SERIES I.

Ingredient	1	2	3	4	5
Spar	0.35	0.30	0.25	0.20	0.15
Whiting	0.15	0.20	0.25	0.30	0.35
Clay	0.65	0.70	0.75	0.80	0.85
Flint	2.10	2.30	2.50	2.70	2.90
Oxygen Ratio	1:3.14	1:3.14	1:3.14	1:3.14	1:3.14

SERIES II.

Ingredient	1	2	3	4	5
Spar	0.35	0.30	0.25	0.20	0.15
Whiting	0.25	0.25	0.25	0.25	0.25
Clay	0.65	0.70	0.75	0.80	0.85
Flint	2.10	2.30	2.50	2.70	2.90
Oxygen Ratio	1:3.07	1:3.10	1:3.14	1:3.19	1:3.23

An inspection of these two tables of equivalents shows that the latter has the advantage by having *three* variable ingredients instead of *four,* but has a variable oxygen ratio, while the former has four variable ingredients and a fixed ratio. All of which shows that absolute elimination of variables is impossible, and that the system of series construction which I generally use and have taught for some years, is after all as little open to objection as any that can be framed. I have myself occasionally made series *by addition,* but for nearly all purposes prefer the substitution method.

In both of the above series, the object planned was to expose the tendency or characteristic behavior of CaO vs. K_2O, and as before stated, I think this can best be done by keeping the oxygen ratio constant and the general type of the body the same. Now, if the object had been to show the effect of changing the fusibility or maturing temperature, then it would have been equally easy to maintain the RO constant and vary the oxygen ratio, thus obtaining a very simple and easily comparable series of trials.

My objection to Mr. Watts' series, was that as it was constructed it gave a series of porcelains in which *both maturing temperature and RO constitution* were varied at the same time, and it was therefore difficult to say to which variation the phenomena were due. In this sense, my criticism was perfectly just. On the face of it, Mr. Watts' series has one variable while in effect it has two.

(3) Regarding the third point, viz., the use of CaO as the sole RO in one end of the series, I think that Mr. Watts' defense of his position is entirely adequate. There was no hope of making a useful porcelain of the composition

$$.15\ CaO \quad 1.\ Al_2O_3 \quad 5.5\ SiO_2,$$

but Mr. Watts knew that as well as any one, and if for the purpose of carrying out the symmetry of his series and of pushing it clearly outside the limits of possible use, he chose to go down to all lime and no potash, no criticism

can properly be made of him for it. In fact, no *serious* criticism *was* made of it in my former remarks. What I said on this point was in the same connection as the matter discussed in section 2, and was chiefly a commentary on the wide extent of his series and the consequent difficulty of interpreting its results, rather than on the use of CaO alone.

(4) On the fourth point, Mr. Watts is unqualifiedly right and I was equally wrong. The use of the three temperatures was necessary to the development of the facts which he had announced at the beginning of this portion of his paper, (p. 608), and as I have repeatedly used the same expedients in my classwork, and in investigation work, it is difficult to see how the statement could have been allowed to creep into print, except from inexcusable haste and lack of careful editing.

(5) I differ with Mr. Watts as to the point made in his fifth topic, and in fact the whole matter has arisen from just this difference in point of view. I think Mr. Watts' data are valuable (in spite of the various criticisms which I have made of it); the facts brought out are good, and are worth while. I thought he should have interpreted the data, as he could have done it better than any one else could possibly do. But in his last words, he specifically threw this task on others. Rather than let the data go un-analyzed, I wrote a digest of it myself. The fact that my conclusion, reached without any pretensions to expert knowledge of the electric porcelain field, should have checked his own expert views, seems to me a sufficient justification for the labor expended on it, and justifies my contention that the data was worth interpreting and that Mr. Watts was the man to do it.

A STUDY OF A TYPE OF MATTE GLAZE MATURING AT CONE 2-4.

BY

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The following study was begun in connection with class work in the Ohio State University, but has been continued as occasion has permitted for the past year or so. The intention in the beginning was primarily to work out a satisfactory formula for a matt glaze to mature at the temperature range indicated in the title, and incidentally to show the relation which such a glaze would bear to equivalent bright glazes. As the work progressed, however, it has led into a study of the causes of the matte quality of the glaze, and something of the limits of composition which glazes of this type may have without losing their commercially desirable quality.

The reasons for choosing this particular temperature range are 1st, that the heat is high enough to permit the formation of matte glazes of durable and permanent character. There are some matte glazes of attractive appearance on the market which are so very basic in character, and composed of compounds so slightly combined by heat, that they are attacked by damp air and efflorescence, and become coated with saline incrustations. Such glazes are a reproach to their maker and to ceramic chemists in general. They are totally lacking in dignity as a ceramic achievement, and should be eschewed by all conscientious workers in this field. There are other low temperature matte glazes of reasonable permanence and undeniable beauty, which are matte by virtue of their strong tendency to crystallize, either in visible or microscopic crystals. These are much less common and are usually still easily destructible glazes, though not decomposed by atmospheric action.

2nd. The heat range is not so high as to make the use of ordinary colorants difficult, or to make the glaze hard to keep in its place or in its matte character.

3rd. There is a genuine need of matte glazes in a number of industries at the heat range of Cone 2-4. They should be cheap, and therefore lacking in lead, or boric acid. They should be resistant to weather, or to ordinary cleansing media, and impervious to water. The makers of terra cotta, roofing tile, enameled brick, heavy sanitary goods such as bath tubs, sinks, etc., and makers of art pottery, tiles, architectural faience and others all need such a glaze for portions of their ware.

Having at that time no specific formula of satisfactory character as an objective, and no previous experience in the production of such a glaze, it was decided to start off with a bright glaze of known character, and by systematic alterations carry it into the field of matteness. When finally reached such a result would have the additional merit of having in a measure explained its own *raison d'etre.*

The type glaze from which the experiments began was

$$\left.\begin{matrix} 0.4\ PbO \\ 0.2\ K_2O \\ 0.2\ CaO \\ 0.2\ ZnO \end{matrix}\right\} 0.35\ Al_2O_3\ \ 2.56\ SiO_2$$

which matures as a bright handsome glaze at from Cone 2 to Cone 6, and which has been used on enameled bricks with good results.

Series I.

The first expedient tried was the gradual reduction of free silica.

The following glazes were made, using the RO elements constant as in No. 1.

No. of the Glaze	RO Elements	Al_2O_3	SiO_2	O. R.	Clay
1	0.40 PbO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	2.560	1 :2.500	.15
2	"	0.35	2.306	1 :2.250	.15
3	"	0.35	2.050	1 :2.000	.15
4	"	0.35	1.793	1 :1.750	.15
5	"	0.35	1.647	1 :1.627	.15
6	"	0.35	1.500	1 :1.460	.15

No. 6 represents the lowest silica that can be gotten, while still using the original amounts of feldspar and clay. By cutting these also, the following additions to the series were made:

No. of the Glaze	RO Elements	Al_2O_3	SiO_2	O. R.	Clay
7	0.40 PbO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.30	1.400	1 :1.47	0.10
8	"	0.25	1.300	1 :1.48	0.05
9	"	0.20	1.200	1 :1.50	0.00

Greater reductions in silica could not be made while retaining the same original RO elements. By changing the latter to a small extent, the following extension to the series was produced:

No. of the Glaze	RO Elements	Al_2O_3	SiO_2	R. C.	Clay
10	0.416 PbO 0.150 K_2O 0.216 CaO 0.216 ZnO	0.15	1.10	1:1.51	0.0
11	"	0.15	1.00	1:1.38	0.0
12	"	0.15	0.90	1:1.24	0.0
13	0.433 PbO 0.100 K_2O 0.234 CaO 0.233 ZnO	0.10	0.80	1:1.23	0.0
14	"	0.10	0.70	1:1.07	0.0
15	"	0.10	0.60	1:0.92	0.0

These glazes were all compounded in small quantities, ground and applied to white wall tile 3x1½ inches, and fired to Cone 4, in a test kiln requiring about 14 hours for a run up to this temperature.

These glazes, beginning with No. 1, form glassy, brilliant surfaces, but are very thick and viscous. They will not hold and cover the surface completely. Also, they do not dissolve their solids completely. At No. 4, a different action can be discerned. Its surface is not so glassy as No. 5, as there are matte patches in a semi-glassy matrix; No. 6 has large matte areas with glassy patches; No. 7 is glassy but not good; No. 8 turning matte; No. 9 glassy, attacking the body; No. 10 a beautiful bright glaze; No. 11 the same; No. 12 the same; No. 13 attacks the body very badly, and is still bright; No. 14 is turning matte, but is not good; No. 15 shows some matte patches and some bright ones.

The series as a whole, shows that with the original RO combination, the mere reduction of silica will not produce a commercial matte, though in No. 6 and again in No. 15, the tendency towards matteness is clearly shown.

These glazes lie fairly smooth on the surface of the tiles, with the exception of earlier numbers, which are high in acid. These draw up into beads.

Series II.

The next line of attack was through the increase of clay; next to reduction in silica, this has been more generally used as a means of producing commercial mattes than any other plan.

In order to determine whether the addition of raw clay could be made to produce a matte by mere overloading in a glaze of this type, and also whether the use of calcined clay, or calcined aluminum oxide, could be employed to introduce alumina, without introducing the shrinkage diffifficulties, which accompany the introduction of large amounts of raw clay, the following series was devised:

No. of the Glaze	RO Elements	Al_2O_3	SiO_2	O. R.	Equivalents clay	Accessory ingredient
9	0.4 PbO 0.2 K_2O 0.2 CaO 0.2 ZnO	0.20	1.20	1:1.50	0.00	use gum for adhesion
8	"	0.25	1.30	1:1.48	0.05	use a little gum
7	"	0.30	1.40	1:1.47	0.10	no gum
6	"	0.35	1.50	1:1.46	0.15	no gum
16	"	0.40	1.60	1:1.45	0.20	no gum
17	"	0.45	1.70	1:1.44	0.25	no gum
18	"	0.50	1.80	1:1.44	0.30	no gum
19	"	0.40	1.60	1:1.45	0.10	.10 Cal. Clay
20	"	0.45	1.70	1:1.44	0.10	.15 Cal. Clay
21	"	0.50	1.80	1:1.44	0.10	.20 Cal. Clay
22	"	0.40	1.60	1:1.45	0.10	.10 Oxide Alumina
23	"	0.45	1.60	1:1.34	0.10	.15 Oxide Alumina
24	"	0.50	1.60	1:1.25	0.10	.20 Oxide Alumina

This series, as the preceding, was applied to perforated white dry-press biscuit tile, and was fired to between Cone 4 and 5. A study of the results shows that with one exception, matteness increases with increase of clay, from glaze No. 9 to No. 18. None of the matts produced, however, are desirable in appearance, and No. 18 is full of large blisters and bubbles.

Glazes 19, 20 and 21 are bright, where raw clay in equal amount produced dull ones. Glazes 22, 23 and 24 give matts of distinctly promising texture, but none of them were smooth enough for use. No. 24 was the best.

Alumina, added in the form of the oxide, seems to exercise a distinctly favorable effect as a producer of matte texture, but it is costly. Clay alone does not give any good matts with this RO base combination.

Series III.

In order to demonstrate the effect of the reduction of lead, with a simultaneous increase of the other fluxing elements, the following series was made:

This series was applied to perforated dry-press white tiles and fired to Cone 4-6 in a gas muffle kiln in about 16 hours. It begins with bright handsome glazes. A considerable amount of silica over and above what was desired, is necessarily present at the beginning of the series, because of the higher feldspar, brought in at the lower end of the series. The glazes become harder and harder, and fail to cover the surface, until the last few are mere globuls of clear glass on the surface of the tile. The glass contains suspended matter. I do not think that these globules would flatten out and cover the tile well, even if given higher temperatures.

It is evident that the dropping out of lead and increase of the other fluxes by symmetrical additions will not bring about the matte texture, at least with this silica and alumina content, since the whole series remains glassy, varying only in infusibility. Whether it might do so at lower silica

or higher alumina ranges has not been developed in this work.

No. of the Glaze	RO Elements	Al_2O_3	SiO_2
25	0.40 PbO 0.20 CaO 0.20 K_2O 0.20 ZnO	0.35	2.03
26	0.350 PbO 0.216 CaO 0.216 K_2O 0.216 ZnO	0.35	2.03
27	0.300 PbO 0.233 K_2O 0.233 CaO 0.233 ZnO	0.35	2.03
28	0.25 PbO 0.25 K_2O 0.25 CaO 0.25 ZnO	0.35	2.03
29	0.200 PbO 0.266 K_2O 0.266 CaO 0.266 ZnO	0.35	2.03
30	0.150 PbO 0.283 K_2O 0.283 CaO 0.283 ZnO	0.35	2.03
31	0.10 PbO 0.30 K_2O 0.30 CaO 0.30 ZnO	0.35	2.03
32	0.050 PbO 0.316 K_2O 0.316 CaO 0.316 ZnO	0.35	2.03
33	0.000 PbO 0.333 K_2O 0.333 CaO 0.333 ZnO	0.35	2.03

Series IV.

The next series was designed to determine the effect of barium in place of lead, as a raw ingredient in the RO. Its tendency to cause bright raw lead glazes to become scummy at ordinary temperatures is well known, and it seemed that if used raw in large amounts it might prove a very useful substance. The series was framed as shown on the opposite page.

This series was given the same conditions as to body, application, and heat treatment. The first glaze, No. 6, is a semi-matte, but glaze No. 34 clears up except for a few specks of undissolved matter; in No. 35 undissolved matter increases; in No. 36, round globules of opaque white glass, surrounded by clear glaze appear; in No. 37 the same, with very narrow margins of clear glaze; in No. 38, the same; in No. 39 discs of opaque white glaze with no clear glaze surrounding them; in No. 40, a glossy white opaque surface; in No. 41 the same. No dull finish at all occurs in the series.

These results were a disappointment. The large quantities of barium oxide did not produce any tendency to mattness. They rather tended to produce a glassy porcelainic structure.

The four series of variations thus far executed have demonstrated several things: 1st, that mere reduction of silica, even to excessively low figures, does not necessarily in itself produce mattness; 2nd, that high alumina does tend to produce it, but of an ugly and difficultly controlled type; 3rd, if the RO elements were properly distributed in the beginning, that the withdrawal of one and replacement by another, or the withdrawal of the most active, and its replacement by equal proportions of all of the others does not produce mattness. The occasional imperfect matt glazes thus far produced came chiefly from reduction of silica and simultaneous increase of alumina, but the surface and texture of these was disagreeable. The next logical step in this study seemed to be the use of unsymmtrical or overloaded RO flux combinations, i. e., the production

No. of the Glaze	RO Elements	Al_2O_3	SiO_2
6	0.4 PbO 0.2 K_2O 0.2 CaO 0.2 ZnO	0.35	1.50
34	0.35 PbO 0.05 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
35	0.30 PbO 0.10 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
36	0.25 PbO 0.15 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
37	0.20 PbO 0.20 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
38	0.15 PbO 0.25 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
39	0.10 PbO 0.30 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
40	0.05 PbO 0.35 BaO 0.20 K_2O 0.20 CaO 0.20 ZnO	0.35	1.50
41	0.0 PbO 0.4 BaO 0.2 K_2O 0.2 CaO 0.2 ZnO	0.35	1.50

of glazes in which fluidity should not be sacrifiecd by use of high alumina, but in which the inherent glassiness of the combination should be kept low by the production of slag-like silicates, high in lime and alumina and low in lead or the alkalies. This idea requires the deliberate abandonment of all of the rules of glaze comporiding to which a study of bright glazes leads one.

Series V.

The first experiment in this line was to try the effect of high lime vs. high zinc oxide in a glaze of the same general type as those used in Series IV, except that a lower alumina and lower silica were used.

No. of Glaze	RO Constituents				Al_2O_3	SiO_2
	PbO	K_2O	CaO	ZnO		
42	0.40	0.15	....	0.45	0.20	1.20
43	0.40	0.15	0.05	0.40	0.20	1.20
44	0.40	0.15	0.10	0.35	0.20	1.20
45	0.40	0.15	0.15	0.30	0.20	1.20
46	0.40	0.15	0.20	0.25	0.20	1.20
47	0.40	0.15	0.25	0.20	0.20	1.20
48	0.40	0.15	0.30	0.15	0.20	1.20
49	0.40	0.15	0.35	0.10	0.20	1.20
50	0.40	0.15	0.40	0.05	0.20	1.20
51	0.40	0.15	0.45	....	0.20	1.20

This series was given the same heat treatment, preparation and body as before. The burning was done in a different firing operation from the four preceding series, but the conditions varied very little.

The following observations were made on the fired tiles:

The high zinc end (No. 42) glave clear glassy glazes, which showed their supersaturation by forming small stellate zinc crystals. These crystals persisted through the upper part of the series to glazes 45 or 46. The middle of the group is a clear and brilliant glass, as was expected, but this persists clear to the high lime end (51), which is

still clear and glassy, except for a transparent scum of very thin, fine bubbles floating on the surface of the glass. Where this scum breaks, as it does occasionally, it shows a beautiful clear transparent glass beneath.

The conclusion to which this series leads is that where as much as 0.4 equivalent lead oxide is employed and a temperature as high as Cone 4 to 6, that bright glazes will still result where the RO is heavily overloaded with either lime or zinc oxide. Obviously, the glass making capacity of the mixture is still too high, and it must be lowered by either reduction of lead or alkalies, or the increase of the aluminum. The latter alternative was first tried.

Series VI.

No. of Gl zes	RO Constituents			Al_2O_3	SiO_2	Clay	Calcined Alumina
	PbO	K_2O	CaO				
53	0.40	0.15	0.45	0.15	1.60	0.00	0.00
54	0.40	0.15	0.45	0.20	1.60	0.05	0.00
55	0.40	0.15	0.45	0.25	1.60	0.10	0.00
56	0.40	0.15	0.45	0.30	1.60	0.15	0.00
57	0.40	0.15	0.45	0.35	1.60	0.15	0.05
58	0.40	0.15	0.45	0.40	1.60	0.15	0.10
55A	0.40	0.15	0.45	0.25	1.60	0.05	0.05
56A	0.40	0.15	0.45	0.30	1.60	0.05	0.10
57A	0.40	0.15	0.45	0.35	1.60	0.05	0.15
58A	0.40	0.15	0.45	0.40	1.60	0.05	0.20

These glazes were fired in the second kiln, at Cone 4-6, as the preceding have been. The results show as follows:

No. 53. A clear, bright, transparent glaze with a thin opaque scum hiding its surface. Very ugly.

No. 54. Less scum, some bright patches.

No. 55. Bright clear glaze containing a little undissolved matter.

No. 56. Bright clear glaze with some undissolved matter.

No. 57. Glazes becoming matte, in patches.

No. 58. A very pretty matte, in patches; flows fairly well, but pin holes badly when too thick. It shows a nice texture in many places.

No. 55A. Bright, beautiful glaze.

No. 56A. Contains a little undissolved matter.

No. 57A. Verging on mattness, but is still a little too glossy.

No. 58A. A nice matte, about like No. 58.

This series shows that a moderately high alumina content is an actual help to the glassy structure, where the RO is heavily over-loaded with lime. The middle of this series makes rather nice clear glazes—much better than the low alumina end, which is scummy. On the other hand, over-loading with Al_2O_3, especially the calcined variety, seems to lead toward matteness.

This series and No. V would have been more instructive if the silica and alumina content had not been varied, but the two were not made and fired in sequence, but together, and the information derived from the study of Series V was not available when Series VI, VII and VIII were planned.

Series VII.

This series was designed to show the effect of replacing lead by barium, in an RO which is over-loaded or unsymmetrical in other respects. This is a companion series to IV, in which the same substitution is tried in an RO properly proportioned for bright glazes. The composition of glazes used was as follows:

No. of Glazes	RO Constituents				Al_2O_3	SiO_2
	PbO	CaO	K_2O	CaO		
63	0.40	0.00	0.15	0.45	0.20	1.60
64	0.35	0.05	0.15	0.45	0.20	1.60
65	0.30	0.10	0.15	0.45	0.20	1.60
66	0.25	0.15	0.15	0.45	0.20	1.60
67	0.20	0.20	0.15	0.45	0.20	1.60
68	0.15	0.25	0.15	0.45	0.20	1.60
69	0.10	0.30	0.15	0.45	0.20	1.60
70	0.05	0.35	0.15	0.45	0.20	1.60
71	0.00	0.40	0.15	0.45	0.20	1.60

This series was fired as in the other cases to Cone 4-6, on same body and heat treatment. It begins with scummy glazes, showing bright and transparent through occasional rifts in the scum, and runs speedily into opaque matte effects (65-66). The series is not fused enough to work well, being porcelainic in many places, and unable to mend defects in the glaze coat by flowage after they once form. Nos. 68 and 69, containing 0.1 and 0.15 lead oxide and 0.25 barium and 0.30 barium oxide, respectively, are the most promising. They have a pretty matte texture, and their only defect is their failure to lie smooth and to cover the surface nicely and uniformly. This is a physical defect which can doubtless be overcome by varying the mode of application.

The three last series, which were framed all at the same time and after the results of the first four series were known, seem to have disclosed some significant clues, and to have produced a few promising glazes. The conclusions which we may deduce are:

1. No high lead glaze (0.4 eq. or near it) gave good matts, except those which were made opaque by calcined alumina.

2. Over-loading with zinc oxide in the presence of high lead (9.4 eqv.) produces clear glazes with zinc crystals instead of matts.

3. Overloading with lime in the presence of high lead (0.4 eqv.) produces clear transparent glazes, obscured by thin layers of scum, or transparent layers of bubbles, but no matts.

4. High alumina, (0.35—0.40 eqv.), either derived from a good deal of clay and a little calcined alumina, or from a little clay and a good deal of calcined alumina readily gives a matt glaze, even where the lead is too high to get a matte otherwise. This observation checks the previous experiences with Series II.

5. Replacement of lead oxide by barium oxide gives a much better effect than in Series IV, where the glass forming ingredients were in good balance. Here, with less

alkali and high lime, the gradually diminishing lead oxide does not find a proper substitute in barium oxide, and a slag is formed, fairly fluid but opaque and matte in character. It seems significant that the best matte texture is reached where a small amount of (0.10 eqv.) lead is present. It probably acts as a starter for fusion, and helps to get other fluxes into action.

The preceding ideas, embodied in one glaze, seemed to indicate the following as about the best basis for further study:

No. 72

$$\left.\begin{matrix}0.05\ PbO\\0.05\ ZnO\\0.15\ K_2O\\0.40\ CaO\\0.35\ BaO\end{matrix}\right\}\ 0.20\ Al_2O_3\quad 1.60\ SiO_2$$

in which 0.15 equivalents of alumina comes from spar and 0.05 from raw clay. This was made up, and also

No. 80

$$\left.\begin{matrix}0.10\ PbO\\0.10\ ZnO\\0.15\ K_2O\\0.35\ CaO\\0.30\ BaO\end{matrix}\right\}\ 0.25\ Al_2O_3\quad 1.60\ SiO_2$$

and a number of others, in which the general type of the RO remained about as above, while variations were confined to silica, alumina and coloring oxides.

At the end of a very considerable amount of work, in which one serial glaze numbers ran up to 157, we felt that we had reduced the case to the following:

1st. That for the heat range which we desired to use, the proportions of the ingredients had been established by the method of gradual exclusion to a range of formula about as follows:

$$\left.\begin{matrix}0.05\text{ to }0.10\ PbO\\0.00\text{ to }0.10\ ZnO\\0.45\text{ to }0.35\ CaO\\0.40\text{ to }0.30\ BaO\\0.15\qquad K_2O\end{matrix}\right\}\ 0.20\text{ to }0.35\ Al_2O_3\quad 1.20\text{ to }1.80\ SiO_2$$

However, in spite of this broad range of composition, and the numerous experiments made, we could not say that a single entirely acceptable matt glaze had been pro-

duced. There were nearly a dozen or two at least which had a nice matt texture, but never a one in which a decently smooth or uniform coat was obtained. The persistence of these formulæ in producing matte textures, the distinct tendency away from mattness whenever these rotios were seriously altered, and the beauty of occasional small patches of one or other of the glazes, all united to convince us that the trouble lay in application or treatment, rather than in composition.

Series VIII.

Experiments were now begun on modes of application. Hitherto all glazes had been ground in ordinary hydrant water. In drying, these glazes nearly always cracked or crazed into small irregular polygonal blocks or sections. On firing these cracks would widen, the edges of the glaze once parted rolled back, gathered up into more or less spherical beads as fusion progressed, finally flattening out and flowing more or less, but seldom if ever covering the original surface smoothly.

The various expedients used for obtaining smooth coats of glazes and engobes were reviewed: 1st, spraying on, instead of dipping; 2nd, use of gum, gelatine, glue, or some similar adhesive to keep the glaze cohering in a film, until such time as the heat began to fuse it; 3rd, use of crystalline salts, such as carbonate of soda, borax, plaster, water, etc., to bind body and glaze together by a net work of fine crystals and thus prevent parting or cracking; 4th, the use of a thin coat of glaze, higher in lead, on the body as a foundation, on which the matte glaze might be expected to flow more easily and thus cover over cracks and defects due to application or drying. No help was gotten from this effort. The use of gum or some other adhesive colloid was thought the best line to try, and incidentally to work in tests on the merits of spraying vs. dipping and the effect of dipping in various way, such as numerous thin coats, a single or a few heavy coats, etc.

The colloid of whose use we had most frequent example in the factories was gum tragacanth. The following data were developed in standardizing its use in our glazes.

Solution of the Gum. The gum comes in opaque white or translucent flakes which soften in water and gradually dissolve. Heating the water and boiling hastens the solution but does not seem to alter the amount which can be taken up. After experimenting on various plans, we finally settled on the plan of soaking the gum in cold water over night and boiling the next day, and finally pouring through an 80 mesh sieve to hold back any undissolved lumps. The solution thus obtained looks like thin starch —having a sort of pearly translucent appearance if concentrated, or like clear water if dilute.

Quantity of Gum. The amount of gum to be used in making a proper solution to give good results is exceedingly small. Experiments began at 50 grams gum per quart water, and this would not anywhere near dissolve. By adding gradually up to five quarts of water solution was reached. This gives 10 grams to the quart as the maximum that can be dissolved. It produces a thick mushy material entirely too thick for glaze purposes.

From this point, successive dilutions were tried, down to one gram to the quart. The latter is too dulute. Its presence in the water can scarcely be noticed, and the glaze remains dusty on the body and can be rubbed off easily, showing insufficient cohesion.

The final decision was to use 3 grams gum per quart of water. Two will do the work fairly and four is higher than need be.

Mode of Incorporation. Experiments were made (a) by grinding glazes in pure water, and adding concentrated gum solution afterwards; (b) grinding glazes in water, settling them, decanting the water as close as possible, and then pour in the gum solution, stir up the glaze and put through screen again; (c) putting dry glaze and dry gum together in ball mill, adding required amount of water, and grinding till solution took place; (d) weighing out dry

glaze batch, putting in ball mill and grinding with gum solution of three grams to the quart, and using same solution to wash out the mill.

Of these methods (d) is far the best. In the other, lumps, curdling, etc., occur, and the thickness or density of the glaze is more difficult to gauge. By preparing and keeping on hand the gum solution in quantity, and of the correct strength, the labor of getting a batch of glaze ready for use—merely using the gum solution as if it were ordinary water, from which it is difficult to tell it.

Quantity of Fluid per Dry Weight of Glaze. In this direction, experiments developed that for glazes of the general nature of those we were using the following rule worked very well, viz.: Use for a unit weight of dry glaze one and one-fifth units of standard gum solution. Use one part of this solution to grind the glaze with in the ball mill, and reserve the one-fifth to wash out the mill, rinse off the pebbles, and clean up the residues on the screen. For 250 grams of glaze, 300 grams of gum solution, after thorough grinding, made a liquid of just the proper density to give a good coat.

For other types of glazes, when the molecular weights are markedly higher, this proportion might not hold; also some ingredients might make a markedly different kind of slip in which this proportion would no longer be serviceable. For ordinary cases, it will probably be convenient.

Mode of application of Gum Glazes. Three methods were tried, viz., dipping, spraying and buttering. The last was tried with thick glaze and with tiles previously partially saturated with water, so that they would not absorb the water from the paste too quickly to get an even spread. This method does not work badly on tile, but as a practical method for factory use is out of the question.

As between dipping and spraying, the advantage is with the dipping so far as speed and convenience is concerned. Spraying may be used for coloring, blending, speckling, and similar purposes, and in this respect, it has no substitute. No other means can possibly duplicate the

beauty and finish which with the air spray is easy. But for straight glazes, of one color, it is not necessary and is much slower than dipping. On one-color, straight work, the sprayed glaze is no more likely to develop a beautiful dappled surface texture than a dipped glaze.

In either spraying or dipping, it is important to have the ware hot, so that the gum glaze may be dried out rapidly to a hard surface. This expedient was found exceedingly useful, and for many kinds of ware it is practical. In some cases it would be prohibitively expensive to heat up the ware before dipping and dry each coat of glaze before another is applied.

Thickness of Coat. In general, matt glaze effects depend for their beauty on a flow or drainage of the glaze from one part of the ware to another. This is especially true of art pottery and tiles. For this reason, matte glazes are usually applied in thick coats, often $\frac{1}{8}$ or even $\frac{1}{4}$ inch. Thin coats of 1-100 to 1-16 of an inch, as are often used with bright glazes, are not often possible with matts. To determine how to create these thick coats, while still keeping their absolute continuity and freedom from cracks, experiments were made with dipping a large number of times, using a thin glaze and drying each coat until hard and the tile hot, versus dipping with a thicker glaze and getting the same body of glaze in one or two operations.

As many as twenty consecutive coats have been applied to tiles, with a thin glaze, and a perfect layer obtained after all. The favorable influence of the gum solution can hardly be better shown than by this fact, for a water-ground glaze would be practically sure to crack during all these heating up and cooling down treatments.

As a result of these tests we found that while admirable results can be gotten from spraying, if sufficient time and enough treatments are given to get a good thick coat, that with gum-solution glazes of proper preparation glazes can be applied in two dippings which are thick enough to develop the matt characteristics and beauty in high degree,

and as this is much quicker and cheaper and applicable to most purposes, this method was used.

Firing Results. Several hundred trial pieces were fired in the prosecution of these experiments. The glazes used were those represented in the foregoing series, and those which gave the best matt effects were such as would fall inside the composition range already given. In brief, we found, after mastering the details of preparation of the gum solution, the proper incorporation of the glaze in it, the fixing of the density of the glaze and the mode of application, that we were able to repeat the same experiments given in some of the preceding glaze series, and obtain from every glaze in the series a smooth and perfect layer, where before not one perfect one could be found.

The status of the work now stood as follows: 1st, we had explored a field of considerable area and found limiting conditions, inside of which matt texture was produced and outside of which the glazes either had less matt texture or became otherwise worthless. None of these glazes gave perfect layers. 2nd, we had found by the use of gum tragacanth, a mode of production of smooth coherent glaze layers, and that with this substance it was possible to produce a very large percentage of perfect results, with any glaze tried, so far as defects of the application were concerned. 3rd, we found that with gum solution, used on glazes inside the limiting range of composition before mentioned, that all of them gave good results.

The foregoing shows that progress had been made, but after all, the work could only be regarded as preliminary. It was merely a reconnaisance—not a survey, of what can be done in this immediate area of glaze composition. With the technique of the process now fairly well in hand, it became necessary to decide on one of two courses to pursue.

1st. To go thoroughly over the field of the RO combinations available and accurately define the area within which the glazes become characteristically matt and of favorable appearance for economic use.

2nd. To study first and very thoroughly the bearing

of the silica and alumina content and the temperature treatment on the matt glaze production, using one type of RO constantly, until the functions of the other elements had been established.

Since the alumina and silica ratios and the heat treatment are necessarily involved in the production of any glaze we might make, the second seemed the better plan, and if any time remained after this point had been exploitd, then the RO problem could be undertaken with the knowledge that our silica and alumina factors and heat treatment were correct.

Series IX.

The RO selected for this new work was a sort of average, or central figure, among the various fairly successful glazes we had made up to this point. It was as follows:

0.15 K_2O
0.10 PbO
0.10 ZnO
0.35 CaO
0.30 BaO

Of this, the potash came from feldspar, the zinc from the oxide, and the lime, barium and lead from the carbonates.

With this single RO combination, we prepared the following series of mixtures, in which the four possible alternatives are used, viz.:

Low Alumina and low Silica.
Low Alumina and high Silica.
Hight Alumina and low Silica.
High Alumina and high Silica.

The serial numbers of the glazes, and their actual contents in alumina and silica are given in the following table:

Molecules of Silica to 1 RO	Al_2O_3 0.15	Al_2O_3 0.20	Al_2O_3 0.233	Al_2O_3 0.267	Al_2O_3 0.30	Al_2O_3 0.333	Al_2O_3 0.357	Al_2O_3 0.40	Molecules of Silica to 1 RO
1.20	249	158	171	184	197	210	223	236	1.20
1.30	250	159	172	185	198	211	224	237	1.30
1.40	251	160	173	186	199	212	225	238	1.40
1.50	252	161	174	187	200	213	226	239	1.50
1.60	253	162	175	188	201	214	227	240	1.60
1.70	254	163	176	189	202	215	228	241	1.70
1.80	255	164	177	190	203	216	229	242	1.80
1.90	256	165	178	191	204	217	230	243	1.90
2.00	257	166	179	192	205	218	231	244	2.00
2.10	258	167	180	193	206	219	232	245	2.10
2.20	259	168	181	194	207	220	233	246	2.20
2.30	260	169	182	195	208	221	234	247	2.30
2.40	261	170	183	196	209	222	235	248	2.40

As may be readily surmised, the left hand column, beginning at glaze 249 and running to 261 was an afterthought, and was aded when partly through with the work, because we found that we had not reached our limits in the direction of low alumina.

The four corner glazes of this series, Nos. 158, 170, 236 and 248 were prepared by weighing out and grinding carefully. They were then screened through a 150 mesh screen, evaporated to dryness on the hot plate, ground and screened again, to break up clots and lumps, and then used as the material from which the other glazes should be prepared by blending.

The blends were calculated in decimal fractions of molecules in which the glazes were to be mixed. Without repeating in detail these figures, the following table shows the mode of procedure:

Silica Content	ALUMINA CONTENT 0.233				
	Glaze Number to be made	Decimal proportion of the four base glazes to be used.			
		Glaze 158	Glaze 170	Glaze 236	Glaze 248
1.20	171	0.833	.....	0.1670	0.0000
1.30	172	0.763	0.069	0.1520	0.0138
1.40	173	0.693	0.013	0.1380	0.0278
1.50	174	0.624	0.208	0.1240	0.0414
1.60	175	0.554	0.278	0.1100	0.0553
1.70	176	0.485	0.346	0.0960	0.0690
1.80	177	0.416	0.416	0.0830	0.0830
1.90	178	0.346	0.485	0.0690	0.0960
2.00	179	0.278	0.554	0.0553	0.1100
2.10	180	0.208	0.624	0.0414	0.1240
2.20	181	0.139	0.693	0.0278	0.1380
2.30	182	0.069	0.763	0.0138	0.1520
2.40	183	0.000	0.833	0.0000	0.1670

Each of these decimal fractions had to be multiplied by the batch weight of the glaze in weighing it out. This again was multiplied by 0.4 to bring the actual quantity of the glaze produced down to a convenient quantity to handle. The computation of glaze No. 180, for instance, was as follows:

0.2080 eq. glaze No. 158×238.3 (batch weight) = 49.56×0.4=19.82
0.6240 eq. glaze No. 170×310.3 =193.62×0.4=77.44
0.0414 eq. glaze No. 236×274.3 = 11.35×0.4= 4.54
0.1240 eq. glaze No. 248×346.3 = 42.94×0.4=17.17

Total 118.97

Each glaze, thus computed, was weighed out in separate portions and the sum of these weights check-weighed, to guard against errors. Each glaze was then put into a ball mill with 1 1-5 times it own weight of gum solution, 3 grams gum per quart of water, ground 30 minutes, strained through 150 mesh and used without any change. No settling, decantation or other change was made in the glaze after coming from the mill. These glazes were applied to biscuited white ware tiles 1½x3 inches, which

were heated up before dipping and dipped while hot. A second coat was applied, with an intermediate drying and heating. Duplicates of each glaze were made. The firing was done in small tile setters, lightly washed with glaze inside—8 tiles per setter, and the setters piled up in a compact block.

The firing was done in a gas-fired muffle test kiln, the heat reached being under close control, and the distribution of temperature being good. Four different burns were carried through, the finishing temperatures, time of burning and time of cooling being:

Burn No. 1—Temperature Cone 2. Time 11 hours. Cooling 12 hours.

Burn No. 2—Temperature Cone 5. Time 12 hours. Cooling 12 hours.

Burn No. 3—Temperature Cone 7-8. Time 14 hours. Cooling 12 hours.

Burn No. 4—Temperature Cone 11. Time 17 hours. Cooling 12 hours.

It is significant, that out of the 183 or 208 tiles in each of these burns that scarcely any imperfect coatings were obtained. The gum solution, as used, seems to completely overcome the beading up, cracks and other defects which made the first work so very unsatisfactory.

The Results. The mass of data is so great that it can only be made comprehensible in chart form, or graphically. The four following charts represent the results as accurately as they can be made to do. Naturally, much is left to interpretation, and no two observers in studying the tiles themselves, would wholly agree as to the classification of some of the tile. The present work, however, was done separately by myself and Mr. W. G. Worcester, and the charts represent the combined judgment in classification of both of us.

CHART NO. 1 - SHOWING CONDITION OF MATT GLAZES OF SERIES IX, AFTER FIRING TO CONE 2.

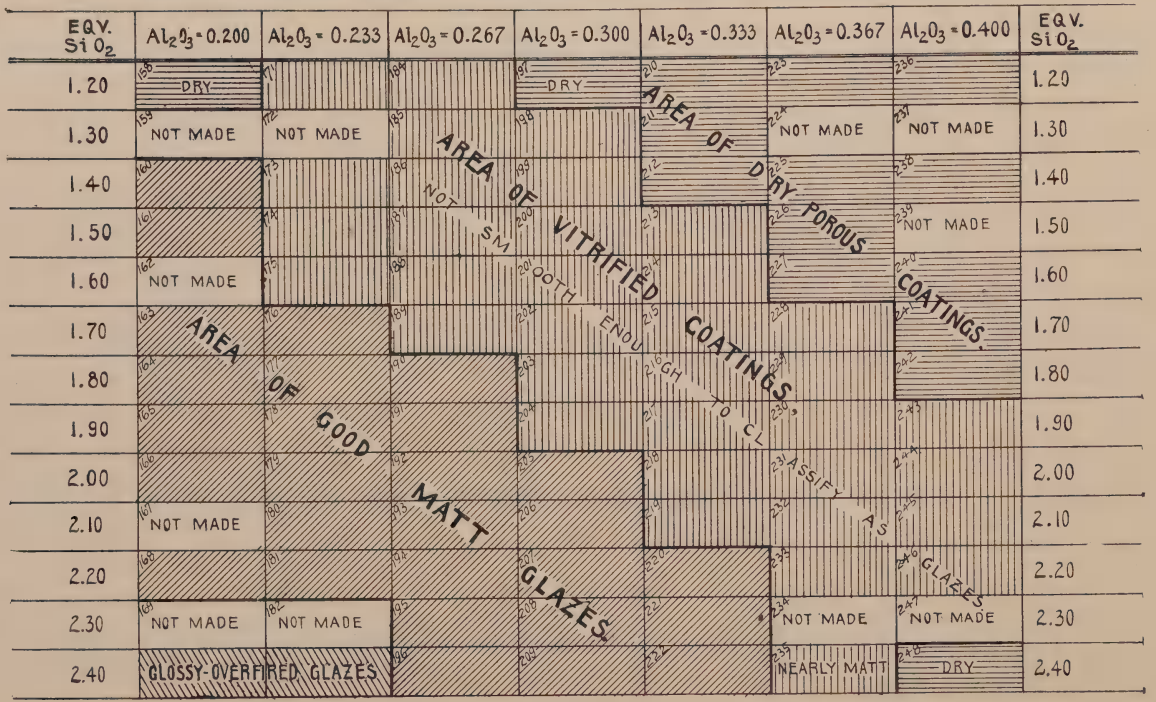


CHART NO. 2. - SHOWING CONDITION OF MATT GLAZES OF SERIES IX, AFTER FIRING TO CONE 5.

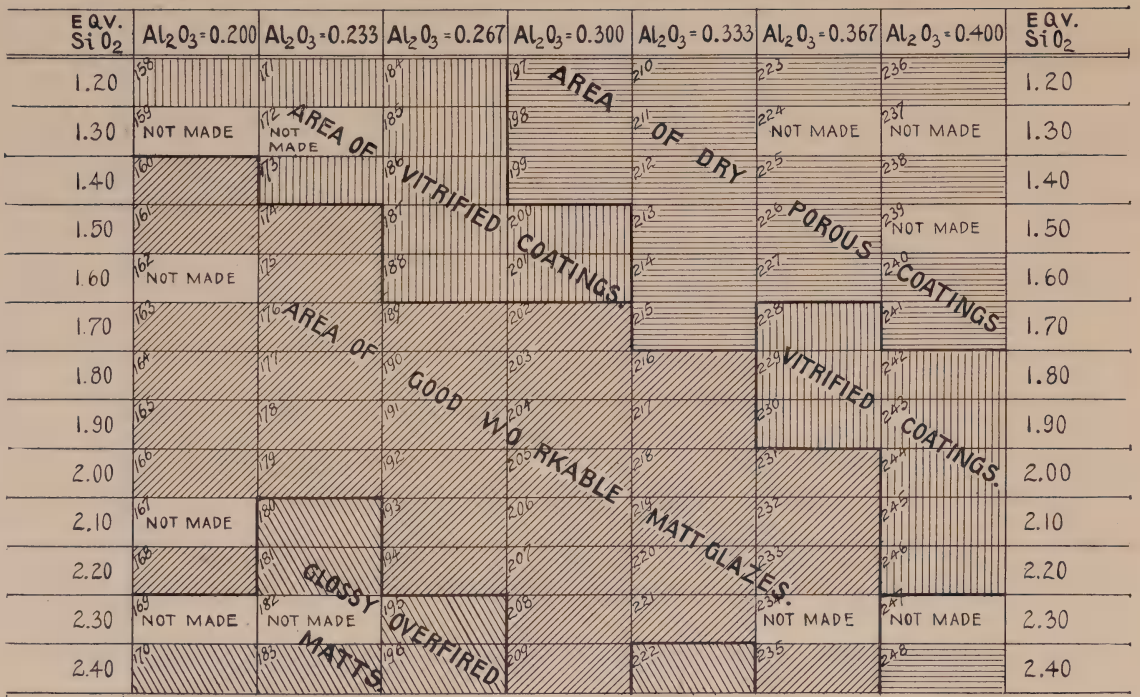
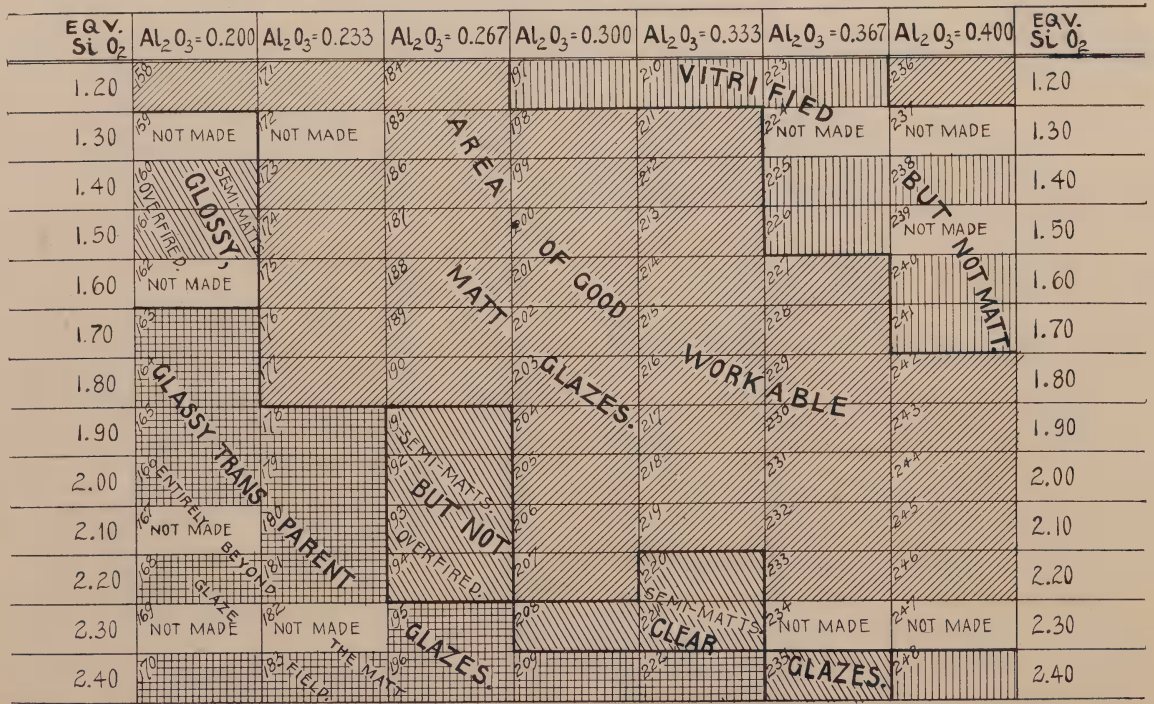


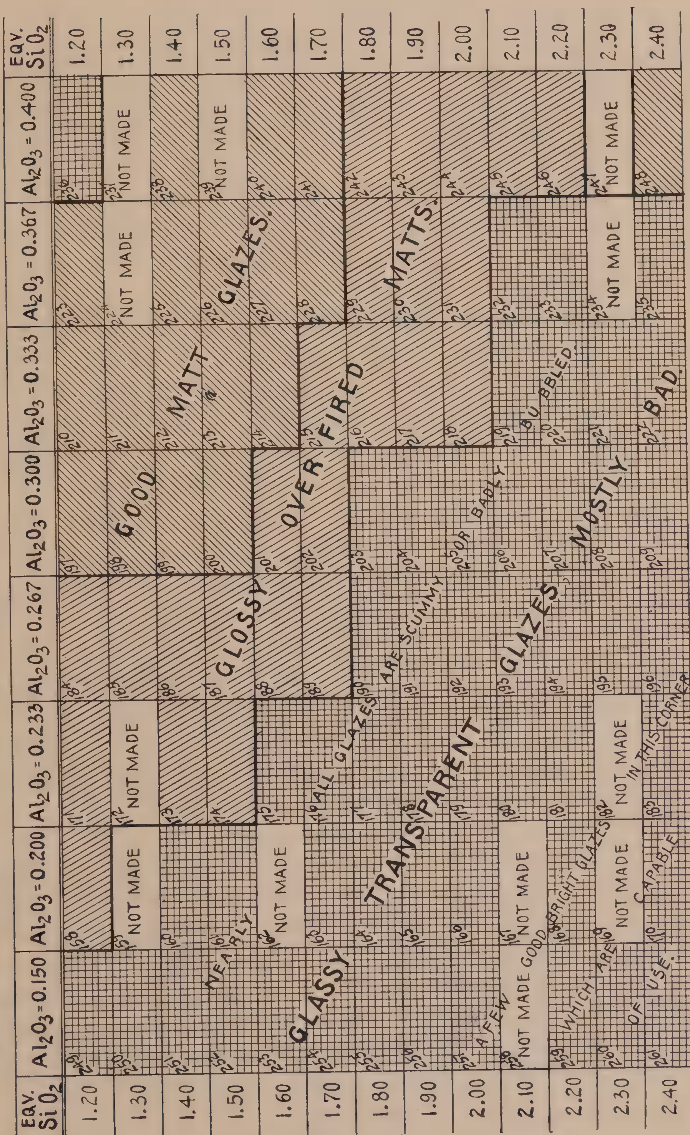
CHART NO.3. SHOWING CONDITION OF MATT GLAZES OF SERIES IX, AFTER FIRING TO CONE 7-8.



TRANS AM CER. SOC. VOL X

ORTON PLATE IV

CHART NO. 4. SHOWING CONDITION OF MATT GLAZES OF SERIES IX, AFTER FIRING TO CONE 11.



Deductions from this Data.

(1) The RO selected is a fairly favorable one. Some beautiful mottled or dappled or "water marked" matt glazes were produced, showing that this glaze is capable on occasion of developing a really artistic surface texture and appearance.

On the whole, though, the glazes averaged less attractive than some of the closely allied matts, like the Van Briggle ware of Colorado Springs, used for art pottery and decorative terra cotta.

On the silica-alumina question, the very interesting and valuable fact has been elicited, that there can scarcely be said to be such a thing as a most favorable ratio or "best" glaze in the whole series. Practically all of the 104 different ratios of silica and alumina for this RO, then, are to be decided with reference to the temperature at which it is desired to mature the glaze, rather than from any inherent tendency of their own.

(3) Mattness in this type of glaze is clearly and definitely shown to be merely *immaturity*. It is a stage through which every one of the glazes must pass in reaching bright fusion. While this matt stage is relatively broad in this type of glaze, and in practice, ware of good texture might be gotten with temperature fluctuations of four or five cones, still it is subject to just the same trouble of "running bright" on overfiring as most of the ordinary commercial matt glazes.

The cause of mattness has been variously interpreted by different writers. Possibly all have been correct in the case of the special glazes from which they have drawn their conclusions. There are unquestionably some glazes which are matt because of an overwhelming tendency to crystallize on cooling, and which flash from the glassy state into the stony state with any cooling treatment which the body could possibly stand, without much regard to the temperaure of firing. Such glazes are, in the experience of the writer, rare and usually are overloaded with stannic oxide.

Alumina has been several times prominently brought forth as the cause of mattness. The present work does not seem to strengthen that claim. The writer believes that alumina in connection with many other oxides, may easily be added in excess in a glaze, and that it acts like any other insoluble matter under those circumstances by tending to make the glaze opaque and matt. But, the writer does not believe that alumina, per se, exercises any strong or profound influence like that of tin oxide towards making glazes inherently matt. It acts merely by making a glaze immature, and this immaturity expresses itself by mattness at one stage and by other surface textures at other stages. Tin oxide does not dissolve appreciably in the glaze at any temperature, and hence a tin matt is generally matt at any stage of fusion where it can be used as a glaze. With alumina the case is otherwise.

(4) Basicity, however, is shown to be a favorable condition if not an actual requirement for good commercial matt glazes. In any single alumina content, within the limits studied, increase of silica has led to glassiness. The point in the series at which glasisness will appear is a function of the temperature, i. e., the maturity of the glaze, but the tendency of higher silica to promote the glassy condition does not admit of argument.

The cause of this now pretty generally admitted fact is not yet clearly known. The fact that it holds true in slags as well as in glasses shows that it is a fundamental or inherent property of silicate salts. What this matt texture is—whether it is the same thing as the stony or crypto-crystalline structure in slags and rocks admits of settlement by work along petrographic lines. Acid silicates, whether they be rocks, or slags, or glasses, or glazes, seem to resist slow cooling while retaining all or large parts of their amorphous glass-like nature. Basic silicates, in the case of rocks and slags and presumably glazes also, seem to possess a strong tendency to crystallize in cooling. By increasing the suddenness of their cooling, the glassy structure may still be kept for a time, but in general the

more basic the silicate, the more difficult it becomes to get it or hold it in the glassy state on cooling.

(5) The relations between immaturity and basicity in determining the physical states of the glaze is very interestingly shown in the charts.

At Cone 2, matt glazes are found with higher silica and lower alumina contents. At Cone 5, the proportion of alumina required to keep the glaze matt has increased, and the amount of silica which it will carry without becoming glassy is distinctly less. At Cone 7-8, still more alumina is needed, and still less silica is tolerated. At Cone 11, only glazes high in alumina and low in silica will produce matts with this RO. All others become bright or glossy.

The center, then, of the matt zone, moves diagonally across the chart beginning with high silica, low alumina, low temperature glazes, and ending with low silica, high alumina, and high temperature glazes.

If, now, we examine the charts with an effort to establish some sort of quantitative ratio to express these facts, and in each column pick out the central glaze, whose mattness is marked favorable or good, we shall get data like this:

From chart 1, glazes fired at Cone 2, we would select as the type glazes, numbers:

164	whose oxygen ratio is	2.25
178	whose oxygen ratio is	2.23
193	whose oxygen ratio is	2.33
208	whose oxygen ratio is	2.42
	Average	2.31

From chart 2, glazes fired at Cone 5, we would select as type glazes, numbers:

163	whose oxygen ratio is	2.12
177	whose oxygen ratio is	2.11
191	whose oxygen ratio is	2.11
205	whose oxygen ratio is	2.10
219	whose oxygen ratio is	2.10
233	whose oxygen ratio is	2.09
	Average	2.10

From chart 3, glazes fired at Cone 7-8, we would select as type glazes, numbers:

187	whose	oxygen	ratio	is	1.66
201	whose	oxygen	ratio	is	1.68
215	whose	oxygen	ratio	is	1.86
230	whose	oxygen	ratio	is	1.90
245	whose	oxygen	ratio	is	1.90
		Average			1.80

From chart 4, glazes fired at Cone 11, we would select as type glazes, numbers:

198	whose	oxygen	ratio	is	1.37
212	whose	oxygen	ratio	is	1.40
226	whose	oxygen	ratio	is	1.43
239	whose	oxygen	ratio	is	1.36
		Average			1.39

Plotting these figures on co-ordinates we have the chart on the next page.

This data emphasizes the facts already brought out and enables us to say with confidence, that *for this RO*, and for others of similar nature and belonging in this class, the oxygen ratios and temperature which will produce matt textures are mutually dependent, and one being known the other may be read off from this curve, or other curves similarly prepared.

Conclusion.

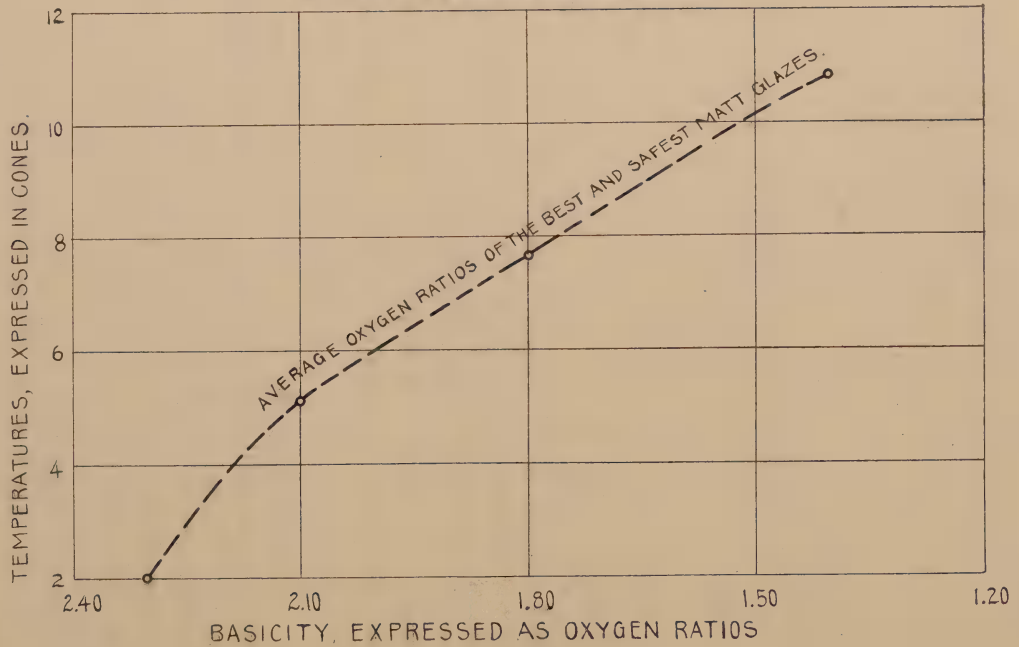
To complete the work which was originally undertaken here, will require a study of the RO combinations on something of the same lines as has been followed in the preceding study of the silica and alumina. This has been undertaken and considerable progress has been made, but it is not yet ready for presentation.

Summing up then the results of the work here published, we may say:

(1) That matt glazes of good texture and ornamental appearance may be produced at temperatures ranging from Cone 2 to Cone 11, and probably a still lower and still higher temperature, within the following ranges of composition:

TRANS. AM. CER. SOC. VOL X ORTON. PLATE V.

SHOWING THE RELATION BETWEEN TEMPERATURE AND BASICITY
IN OBTAINING A MATT STRUCTUE
IN GLAZE WITH CONSTANT RATIO.



$$\left.\begin{matrix} 0.05 \text{ to } 0.10\ PbO \\ 0.05 \text{ to } 0.10\ ZnO \\ 0.10 \text{ to } 0.20\ K_2O \\ 0.45 \text{ to } 0.35\ CaO \\ 0.40 \text{ to } 0.30\ BaO \end{matrix}\right\} \quad 0.20 \text{ to } 0.40\ Al_2O_3 \qquad 1.20 \text{ to } 2.40\ SiO_2$$

(2) That increase of the lead or alkalies, and reduction of the alkaline earth or alumina, tends to bring about a glassy structure.

(3) That increase of silica in any glaze belonging to this category, especially if accompanied by higher temperatures, tends to produce glassiness.

(4) That alumina does not appear to have inherent power to produce mattness, different from that of the alkaline earths and possibly zinc oxide.

(5) That mattness in glazes of the type shown in (1) seems to be a function of the maturity of the glaze, and that so far as we have gone, all these matt glazes are capable of forming bright transparent and permanent glazes, where the temperature is sufficient.

(6) That the maturity of the glaze (and therefore its mattness) is direcaly a function of its oxygen ratio, and the temperoture. Either one of these factors being known, the other may be determined from the charts or from the curve given in Plate V. Assuming an alumina content and a temperature of firing, the correct silica content may be read off. Assuming a silica and alumina content, the correct temperature may be read off.

It is hoped that further work on this line by others may serve to extend the range of compositions to which these principles are known to apply, and also to confirm such of the above generalization as may now seem to rest on too little evidence.

DISCUSSION.

Mr. Mayer: Mr. President, I never made any matt glazes for commercial purposes. I have made some few experiments, and any work I have done along that line has been in the direction of increased alumina. I have no figures or data, but I remember I got up exceedingly high.

It seemed to me that the ordinary glaze with excess of alumina produced a very good matt glaze—simply taking the ordinary glaze and loading it up pretty well with alumina. Outside of that I have not experimented at all.

Mr. Hottinger: I do not know whether I want to discuss a paper of that kind without some study. It seems to me the accepted theory of making matts is taking any glaze and putting alumina in it. The type of glaze which Professor Orton gives, the latter types, I do not know anything about. I never experimented in that direction.

Mr. Binns: I have had quite a series of experiences in matt glazes of many types. In fact, I think I was responsible for the theory that the constitution of matt glazes consisted in the formation of aluminates in mutual solution with the silicates. Nothing which Professor Orton has said has led me to change that view. I have not seen the samples, but my experience has shown me this, that a matt glaze is always hungry for silica. It does not matter much what the basic content is, but if you expose a matt glaze to a surface from which it can dissolve silica, it will turn itself into a characteristic bi-silicate and turn bright; and especially if the ware is glazed somewhat thinly. In order to secure the constitution and quality of a matt glaze, it must be piled as thickly as possible on the ware. I do not believe a matt glaze, if it is quite thin, has the true nature of a matt,—an overcharged glaze, fusible under other conditions, or an immature glaze, which amounts to the same thing. The oxygen ratio pointed out in my first paper still obtains within very narrow limits. The first ratios Professor Orton put on the board are both sesquisilicates. That ratio, within very narrow limits, will constitute a matt glaze. But if put on thinly, it will become bright. I have made many matt glazes, and all are constructed on that principle.

I noticed that Professor Orton stated that he used barium oxide.

Mr. Worcester: We used barium carbonate.

Mr. Binns: Professor Orton said oxide. If you will

consult a chemical authority you will find that barium clings to carbon dioxide with great tenacity. It is more difficult to drive away carbon in combination with barium than with calcium. If you make up a fritt with calcium and another fritt with barium, the barium will melt more quickly than the calcium; but if you make a raw glaze of the barium carbonate, and one of the calcium, the calcium will fuse more quickly. I account for it by the fact that it is very difficult to remove carbon dioxide from barium. For that reason, I found that barium departs from the rule I stated. That is, while keeping somewhere near the ratio used, you must use a lower silica-alumina content where the glaze contains barium than where it does not. This I think will account for some of the somewhat erratic behavior noted. This will no doubt be brought out somewhat further when Professor Orton prepares his paper for publication.

Mr. Stull: Concerning Professor Binns' statement that mattness is due to the formation of aluminates, it seems to me that the aluminates are very unstable, except the spinels formed at high temperatures. Now, I have completely dissolved the glazes off from two beautiful matt vases bringing high prices in the market. I think I can show a matt trial which contains no alumina, and two molecules of silica and one RO. Another thing I can show is matt glazes with two silica and no alumina, and .3 tin. I would like to ask Prof. Binns to explain how this is possible if mattness is due to the formation of aluminates?

Professor Binns: I do not want to be construed as saying that matt glazes are never formed of anything else but aluminates. The first case cited by Mr. Stull is a case of crystallization. In the second, with tin, we have in all probability a form of crystallization also.

Mr. Stull: The glaze with the mattness due to the presence of tin matured at Cone 05. The one which had neither tin nor alumina and two of silica, matured at Cone 7; and neither one could be dissolved with acid. My idea of a true matt is a crystalline glaze, one that has a wide

range of temperature, which cannot be said of highly basic matt glazes. A true matt glaze is a glaze which fuses and has a certain degree of flow and in cooling crystallizes, producing a beautiful, silky, satiny, matt surface. Such a glaze I have made which had a range of two and a half cones and was still good. The trials, if drawn and cooled quickly, were brilliant; if cooled slowly, they were a beautiful matt.

Mr. Plusch: Along the line of Mr. Stull's remarks, in terra cotta work, if we cool our matt glazes too quickly we get bright glazes, if cooled slowly we get a true matt and crystalline. The substitution of low atomic weight RO's for those of higher atomic weight produce better matt glazes, i. e., Na_2O for K_2O, of MgO for BaO.

Mr. Stull: The statement made bears out a law which I laid down in my notes on crystalline glazes. That law said that those metals of low atomic weight whose oxides go to make up the RO, produce the best crystals. Mr. Plusch states that you get better matts by using magnesium oxide and by replacing potash with soda. Purdy and Krehbiel also verify that law by saying that soda produces better crystals than potash.